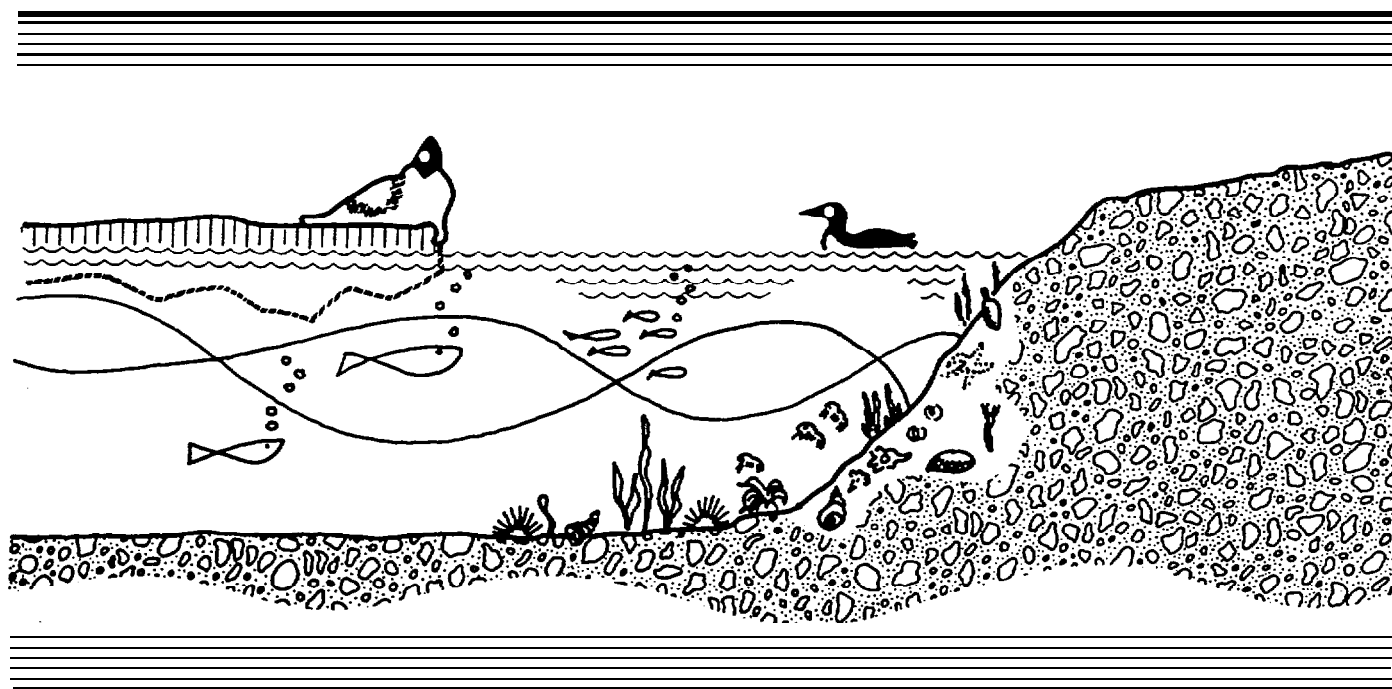# CHEMISTRY

2. Analytical Biogeochemistry

Baffin Island Oil Spill Project

WORKING REPORT SERIES

1981 STUDY RESULTS

BIOS
CAPE HATT

The Baffin Island Oil Spill Project

OBJECTIVES

The Baffin Island Oil Spill (BIOS) Project is a program of research into arctic
marine oil spill countermeasures. It consists of two main experiments or
studies. The first of these, referred to as the Nearshore Study, was designed
to determine if the use of dispersants in the nearshore environment would
decrease or increase the impact of spilled oil. The second of the two
experiments in the BIOS Project is referred to as the Shoreline Study. It was
designed to determine the relative effectiveness of shoreline cleanup
countermeasures on arctic beaches.

The project was designed to be four years in length and commenced in 1980.

FUNDING

The BIOS Project is funded and supported by the Canadian Government (Environment
Canada; Canadian Coast Guard; Indian and Northern Affairs; Energy, Mines &
Resources; and Fisheries & Oceans), by the U.S. Government (Outer Continental
Shelf Environmental Assessment Program and U.S. Coast Guard), by the Norwegian
Government and by the Petroleum Industry (Canadian Offshore Oil Spill Research
Association; BP International [London] and Petro-Canada).

WORKING REPORT SERIES

This report is the result of work performed under the Baffin Island Oil Spill
Project. It is undergoing a limited distribution prior to Project completion in
order to transfer the information to people working in related research. The
report has not undergone rigorous technical review by the BIOS management or
technical committees and does not necessarily reflect the views or policies of
these groups.

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Correct citation for this publication:

Boehm, P.D., Fiest, D.L., and Hirtzer, P., 1982, Chemistry: 2. Analytical
Biogeochemistry – 1981 Study Results. (BIOS) Baffin Island Oil Spill Working
Report 81-2: 354 p.

BAFFIN ISLAND OIL SPILL PROJECT

Chemistry Component -

Report on 1981
Oil Spill Experiment

Vol. 2:

Summary of
Analytical Biogeochemistry

Final Report

Contract No.
(0ss81-00086)

Prepared for:

Environment Canada
Environmental Protection Service
Edmonton, Alberta T5K 2J5

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(under subcontract to
Seakem Oceanography Ltd.)

September 1982

TABLE OF CONTENTS

SECTION ONE

SECTION ONE

INTRODUCTION

1.1 Project Goals

The chemistry component of the Baffin Island oil spill (BIOS) project involved several tasks during the second year of the project:

1. Monitoring petroleum levels in the water column in real-time during the spills (see Volume 1).

2. Establishing the transport paths, fates, and weathering of oil in the four bays in the various basic environmental compartments (i.e. , water column, **benthic** sediments, organisms, shoreline) during the immediate post-spill period (2 weeks).

3. Performing chemical measurements of the oiled shoreline plots (shoreline study) to determine concentration and composition of residual oil.

A tailored analytical program combining analytical property measurements, i.e., ultraviolet fluorescence (UV/F) to determine oil concentrations in the various environmental components, with detailed compositional measurements, i.e. , glass capillary (fused silica) gas chromatography (GC^2), and computer-assisted gas **chromatographic** mass spectrometry (GC^2/MS), to give detailed compositional information, was to be utilized. Thus an important goal of the project was to take the large sample set and blend it into a cost-effective hierarchical analytical scheme to optimize use of the resulting data.

The specific goals of the analytical chemistry program are given in Table 1-1.

TABLE 1-1

HYDROCARBON BIOGEOCHEMISTRY (YEAR 2) GOALS

---

1. To compare the **biogeochemical** fates of chemically dispersed versus surface spilled oil.

2. To examine the composition of low and high molecular weight petroleum components in the water column of the four bays, and to examine the changing composition with time (i.e., weathering).

3. To examine the chemical nature and weathering of residual surface oil and beached oil.

4. To explore the compositional fractionation of water-borne oil into dissolved and particulate classes.

5. To examine the transport of oil to the bottom sediments and related compositional changes through sediment-trap samplings.

6. To analyze bottom sediments for oil content, composition, and weathering changes and to examine the relation of bulk sediment hydrocarbon chemistry to that of the newly deposited surface flocculent layer.

7. To examine the acquisition, assimilation, and **depuration** of petroleum residues by several species of benthic marine organisms, and to examine how these processes varied by species, by bay, and with time (0-2 weeks).

1.2 Technical Plan

The analytical plan used in this study involved the sample types shown in Figure 1.1 and the types of analyses shown in Figure 1.2. The rationale for each type of analytical procedure is presented in detail in Section Two of this report . The overall plan was to carefully blend analytical techniques of varying sophistication and resolution to best enable the program goals to be achieved within budgetary constraints. Such blends have been successfully employed previously in this (Boehm 1981a) and other programs (Boehm et al., 1982a).

1.3 Background

1.3.1 Pollutant Compounds in the Arctic

Although an abundance of data is not readily available, several studies have been undertaken in recent years to determine levels of organic pollutants, most notably petroleum hydrocarbons (PHC), in remote and/or undeveloped arctic marine environments. A general picture emerges of an environment with very low levels of hydrocarbons, but one that is not free from "contaminants" distributed on a global basis by natural and anthropogenic processes.

Wong et al. (1976), Shaw et al. (1979), Shaw and Baker (1978), and Johansen et al. (1977) have investigated petroleum hydrocarbon pollutant distributions in the offshore Beaufort Sea, the nearshore Beaufort Sea, the Port Valdez nearshore environment and the West Greenland coast, respectively. There is little indication in any of these studies of chronic petroleum-related inputs of hydrocarbons,
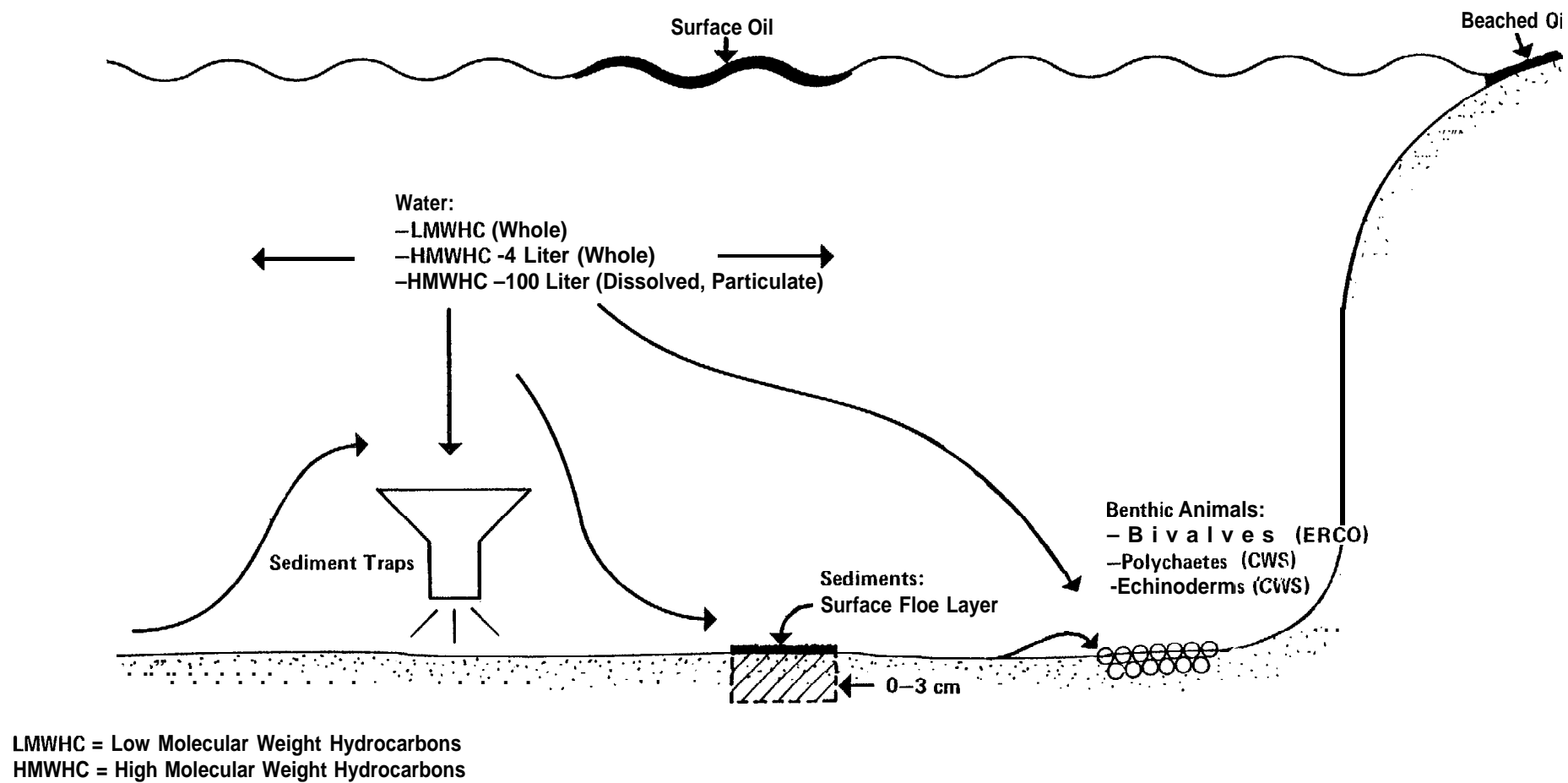
Figure 1.1. **Sample** Types Acquired for BIOS Chemistry Studies (Nearshore Study).

Sample Type

| Oil Samples
—Beached
—Floating | Sediment Traps | Seawater
—LMWHC
—HMWHC | Sediments and Floc | Tissues |

Information Need

| —Weathering
—Detailed Chemistry
—Concentrations | —Weathering
—Detailed Chemistry
—Concentrations | —Weathering
—Detailed Chemistry
—Concentrations | —Presence of Oil
—Concentration Survey
—Detailed Chemistry | —Presence of Oil
—Concentration Survey
—Detailed Chemistry |

Analytical Methods

UV/Fluorescence

—Capillary Gas Chromatography (GC)

—Capillary Computer Assisted Gas Chromatographic Mass Spectrometry (GC/MS)

Figure 1.2. BIOS Analytical Protocols.

although Shaw et al. (1979) suspect that fossil-fuel-related arenes (aromatic hydrocarbons) from coal outcrops or natural seeps are sources for low levels of sedimentary arenes found at several locations. More recently, Levy (1979; 1980) has documented the inputs of petroleum to the Baffin Bay area through natural seepages of petroleum.

Long-range transport of **polycyclic** aromatic hydrocarbons (PAH = arenes) from pyrolytic sources (i.e. , combustion of fossil fuels) is a probable cause of observed distributions of low levels of PAH found in the Arctic (**Wong** et al., 1976; Shaw et al., 1979) and elsewhere on a global scale (**Laflamme** and Hites, 1978; Lunde and **Bjorseth,** 1977).

Some PAH compounds are also produced **diagenetically** (i.e., after deposition of precursors in the sediment) in surface sediments and may therefore not be related to any pollutant sources. Wakeham et al. (1980), Aizenshtat (1973), and Simoneit (1977a, **1977b),** among others, describe the diagenetic production of **PAH** compounds including the more commonly encountered retene **(1-methyl-7-isopropylphen-** anthrene) and **perylene,** and other compounds (e.g. , alkyl- phenanthrenes) that have pollutant sources as well.

There is little evidence indicating that any arctic environment has had sufficient input of saturated petroleum hydrocarbons to mask natural saturated hydrocarbon profiles consisting of marine and terrigenous biogenic compounds. Alkane compositions suggest **biogenic** sources (**Shaw** et **al.,** 1979).

1.3.2 Weathering of Petroleum in the Marine Environment

"Weathering" of oil at sea pertains to that collective set of processes which alter the chemical composition of petroleum through evaporation, dissolution, photochemical oxidation, microbial degradation, and auto-oxidation. The physical processes mediating the chemical changes are mixing, emulsification, and sorption (NAS, 1975; Boehm, 1981b). A schematic diagram of the processes of weathering of surface oil is shown in Figure 1.3. Dispersed oil would initially be influenced to a large degree by water column processes and movement, rather than by evaporation at the air-sea interface or other sea surface processes.

Incorporation of petroleum into the sediment usually results in accelerated weathering of oil in oxygenated substrate, mainly through microbial degradation (Teal et al., 1978; Cretney et al., 1978; Keizer et al., 1978; Beslier et al., 1981; Atlas et al., 1981; Boehm et al., 1981). Boehm et al. (1981) have conducted a comprehensive study of how Amoco Cadiz oil changed markedly in its composition with time after deposition in intertidal sediments (Figure 1.4). Oil buried beneath the aerobic zone is subject to little or very slow anaerobic degradation (Ward and Boehm, unpublished data). Oil may be transported to the benthos by several processes illustrated in Figure 1.5. In the case of chemical dispersion of oil, the magnitude of incorporation of oil into the benthos after dispersion is unknown. Therefore, oil transported to the benthos in small to moderate quantities can be expected to lose much of its obvious fingerprint if the hydrocarbons are available to microorganisms and if abundant amounts of nutrients are present. The paraffinic fraction is altered by oxidation and isomerization first, followed next by the aromatic fraction. Oil which has been highly weathered requires study by sophisticated and extensive analytical
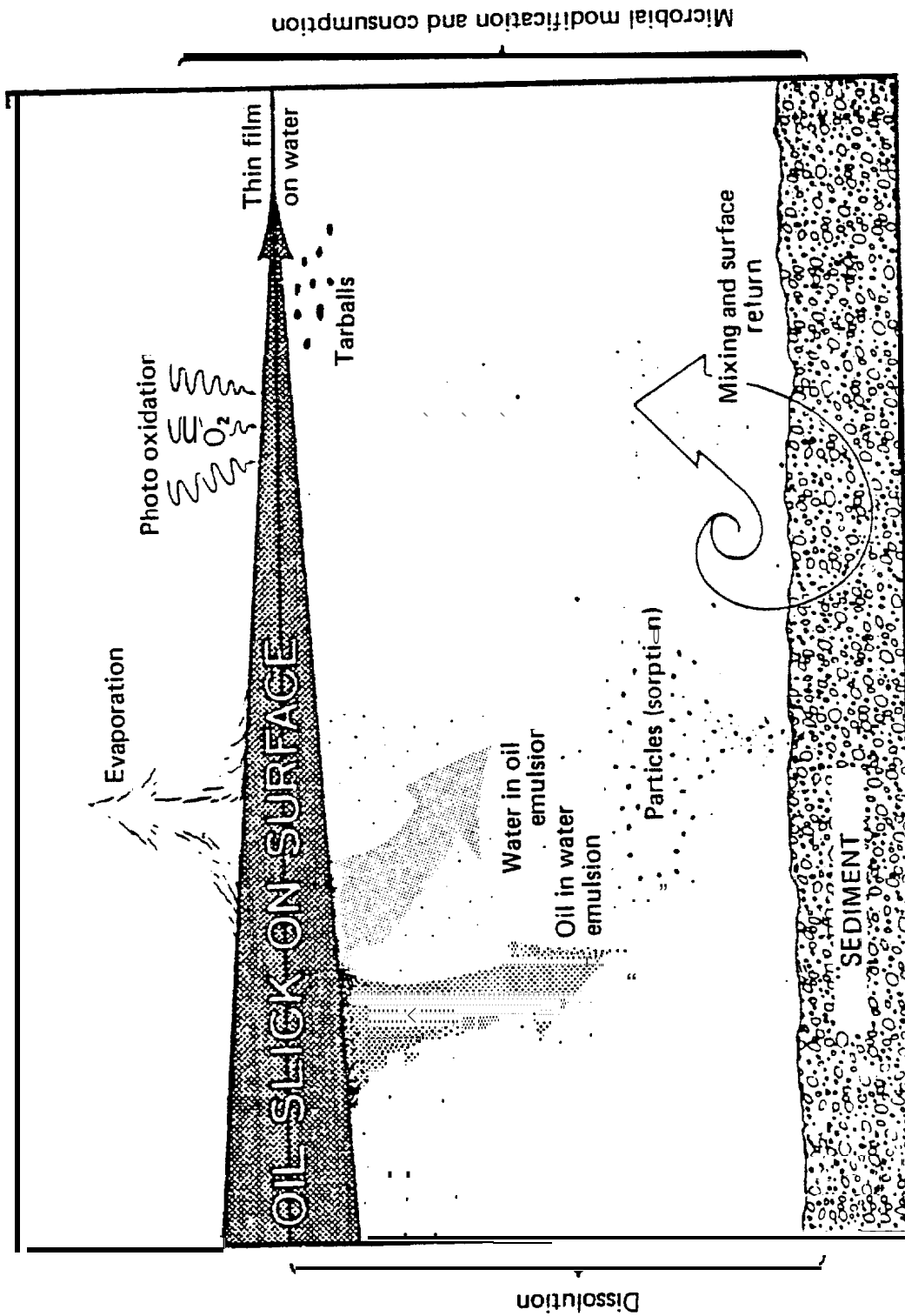
4 REFERENCE MOUSSE (Saturated Hydrocarbons)
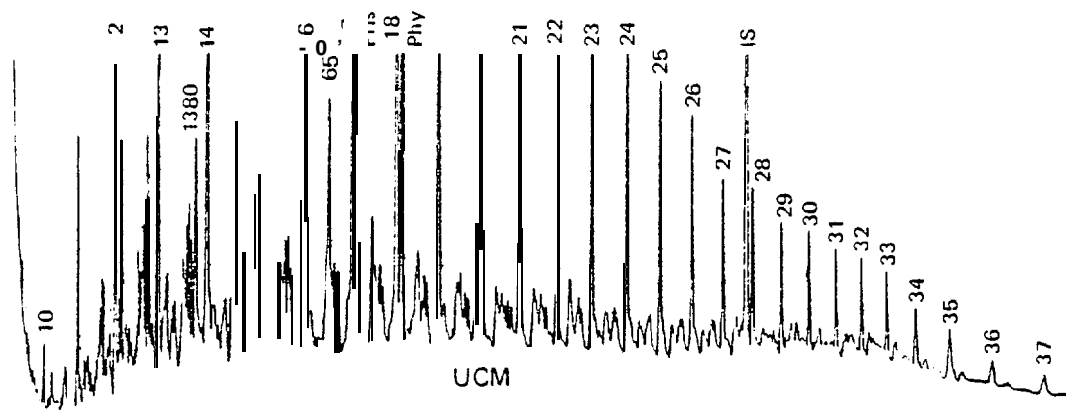
B STAGE 1 WEATHERING (Saturated Hydrocarbons)
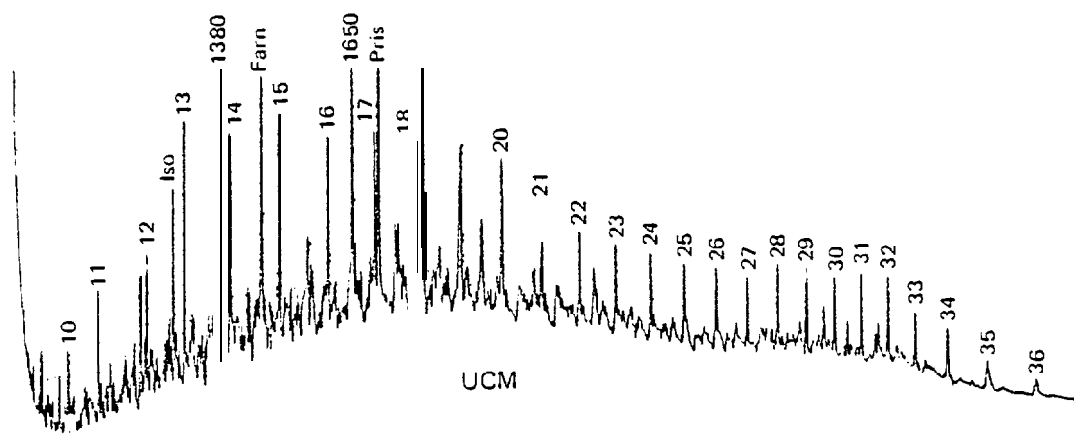
⊃ STAGE 2 WEATHERING (Saturated Hydrocarbons)
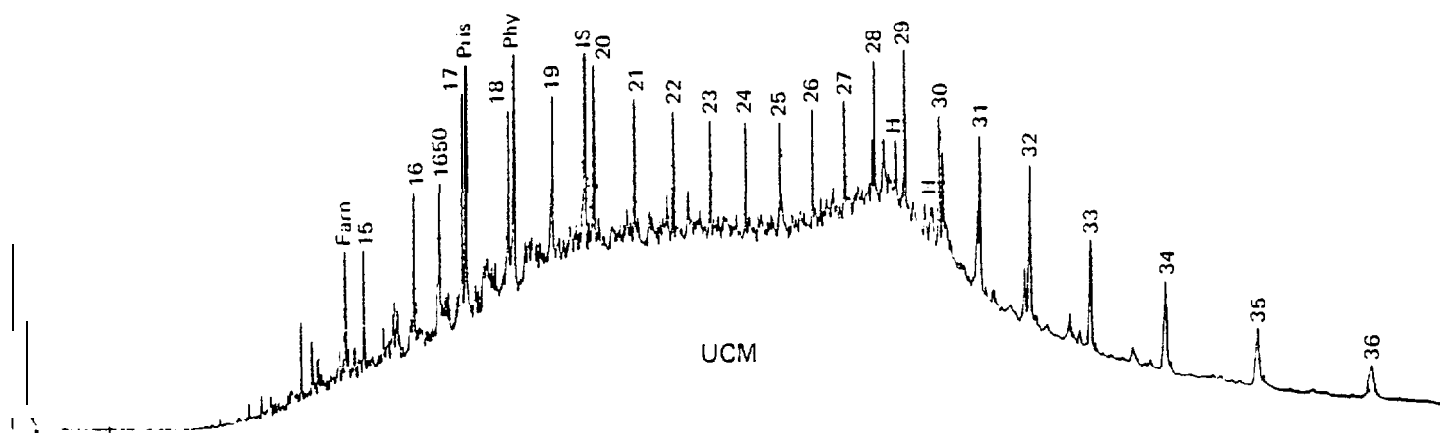
Figure 1,4. Weathering patterns of saturated hydrocarbons in *Amoco Cadiz* oil (from Boehm et al., 1981).

STAGE 3 WEATHERING (Saturated Hydrocarbons)

STAGE 4 WEATHERING (Saturated Hydrocarbons)
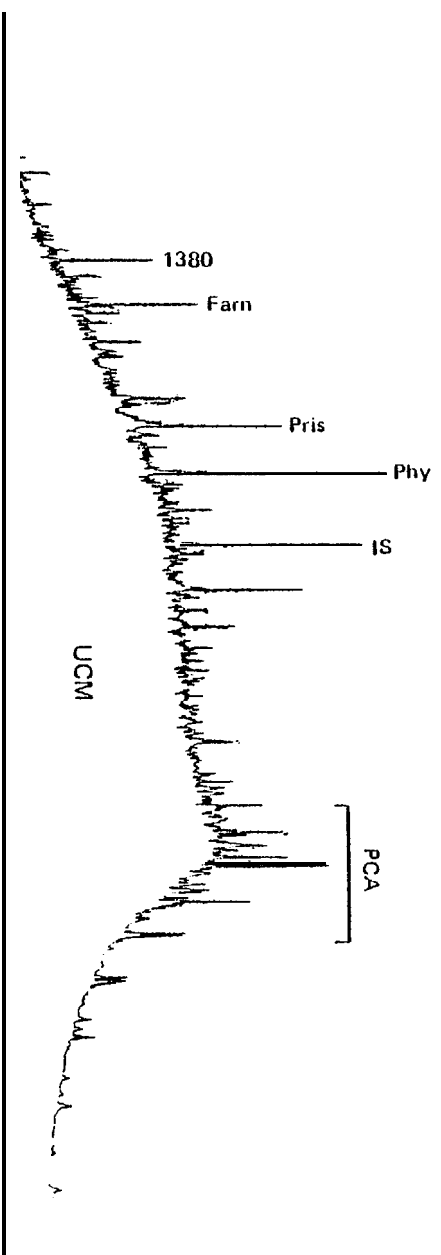
STAGE 5 WEATHERING (Saturated Hydrocarbons)

PCA=Polycyclic Aliphatics
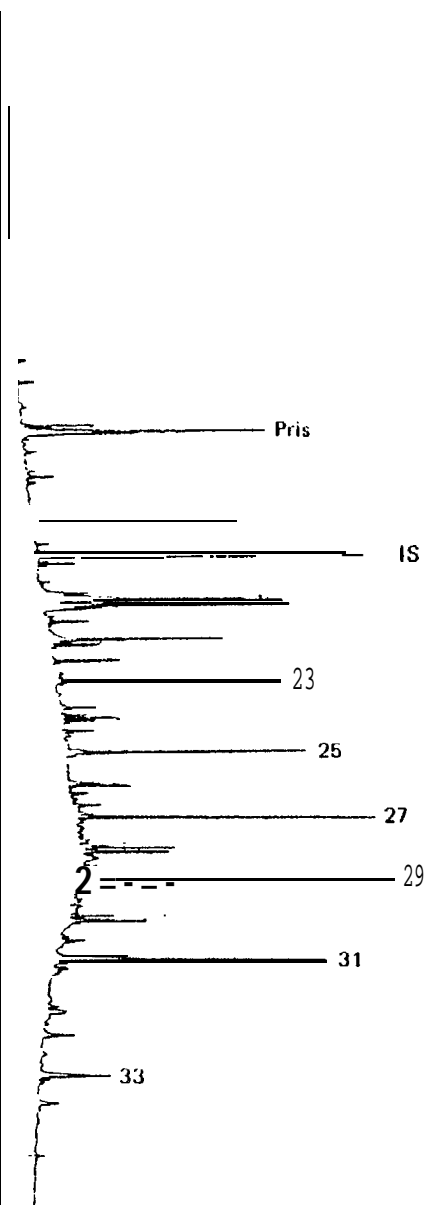
Figure 1.4. (Continued)
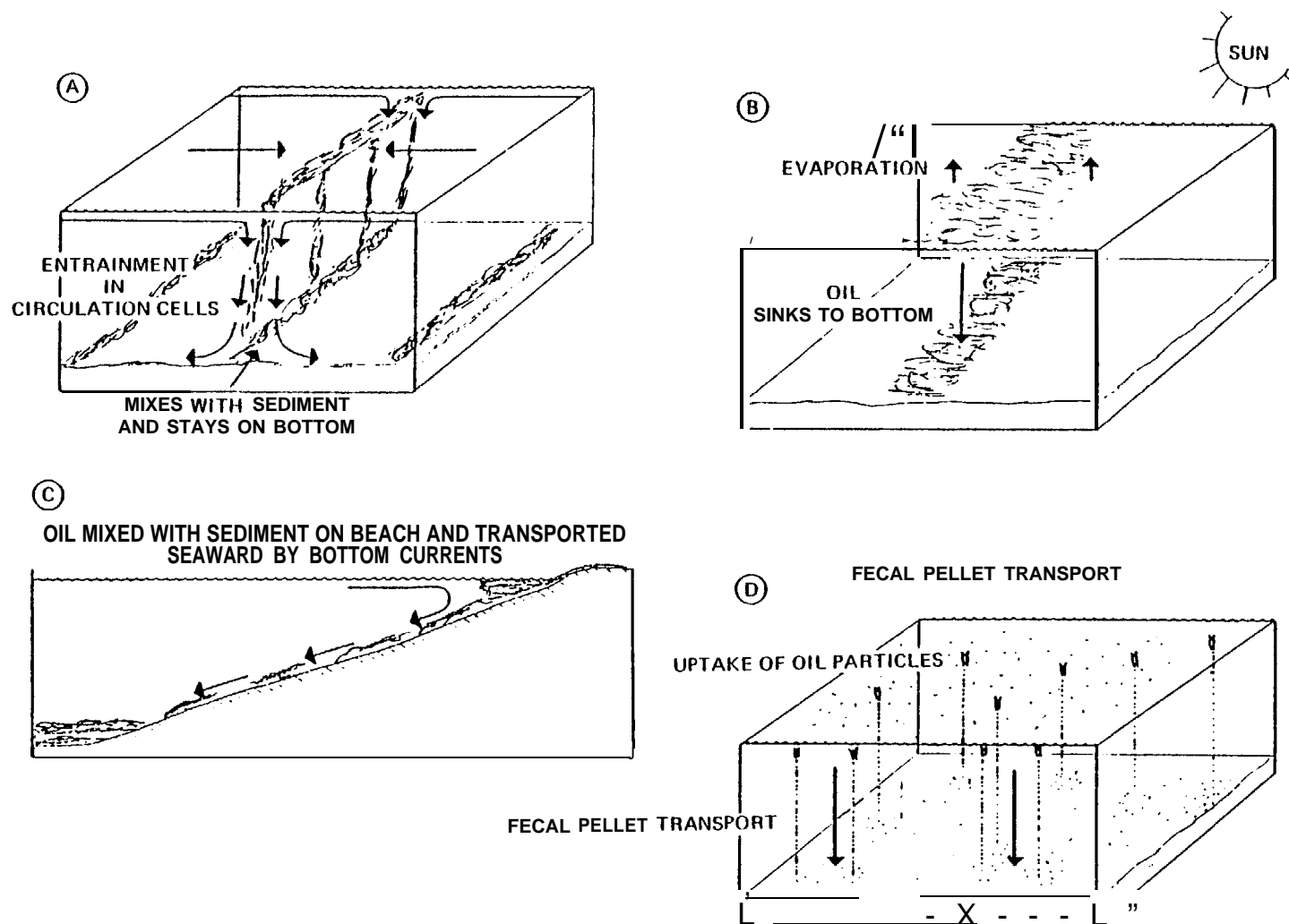
Figure 1-5. Hypothesized Methods by which Oil may be caused to Sink and Remain on the Bottom.

procedures prior to successful characterization. Pelagic
tar balls are exceptions to this rule, maintaining charac-
teristic paraffinic patterns for considerable periods
of time (Butler et al., 1973).

Molecular marker compounds have been used for the
long-term identification and detection of oil residues.
These compound classes are more resistant to environmental
degradation than the more commonly used fingerprintable
material (i.e., **alkanes**). Of particular interest have been
pentacyclic triterpanes (**Dastillung** and **Albrecht,** 1976;
Boehm et al., 1981; Atlas et al., 1981), and **alkylated**
phenanthrenes and dibenzothiophenes (**Boehm** et al., 1981,
Boehm et al., 1982a, Teal et al., 1978). Use of these
markers requires their characterization in the source
material, the **pre-spill environment,** and the post-spill
contaminated samples.

1.4 Summary of 1980 **(Pre-Spill)** Results (First-Year Study)

-The goals of the first year study (see **Boehm,** 1981a)
were to fully characterize the Lagomedio oil used in the
study and to determine the baseline levels of hydrocarbons
in seawater, sediment and tissue from the Ragged Channel and
Z-Lagoon areas. The results can be summarized as follows:

1.   The oil was characterized as a high-Vanadium waxy
     crude having the chemical and physical properties
     shown in Tables 1-2, 1-3, 1-4, 1-5, and 1-6.

2.   Seawater samples were "clean" with respect
     to petrogenic hydrocarbons, but 1-2 rig/liter **of**
     petroleum hydrocarbons were detected in large
     volume (200-liter) samples.

3.   Sediment samples contained marine and terrigenous
     biogenic hydrocarbons, but low levels
     (l-4 ppb = rig/g) of pyrogenic **polynuclear** aromatic

GROSS CHEMICAL CHARACTERIZATIONS OF LAGOMEDIO
CRUDE OIL AND OIL/COREXIT 9527 MIXTURE

SAMPLE	% Saturates	% Aromatics	% POLARS[a]	% RESIDUAL[a]	% ASPHALTENES[b]
Fresh (unweathered) oil	59.1	35.2	6.3	0	1.2
Aged oil	58.8	30.0	14.8	0	2.5
Aged: dispersant (10:1)	44.2	27.5	24.7	3.6	ND

[a]Determined from silicic acid column chromatographic fractionation;
f_1 = hexane eluate; f2 = hexane:methylene chloride (60:40) eluate;
f3 = methanol eluate; residual = material not eluting off column.

[b]Asphaltenes = pentane-insoluble material. Note: asphaltenes may elute
in both f2 and f3 fractions.

ND = not determined

TABLE 1-3

SATURATED AND AROMATIC HYDROCARBON PARAMETERS
OF LAGOMEDIO CRUDE OIL[a]

	FRESH OIL	AGED OIL
Saturates		
SHWR	2.87	2.28
ALK/ISO	2.36	2.50
PRIS/PHY	0.85	0.74
PRIS/n-C_{17}	0.51	0.38
PHY/n-C_{18}	0.61	0.62
Aromatics		
AWR	4.29	3.47

[a]Key:

$$SHWR = \frac{(\Sigma \text{ n-alkanes; } C_{10}- C_{25})}{(\Sigma \text{ n-alkanes; } C_{17}-C_{25})}$$

$$AWR = \frac{(\text{Alkyl Benzenes + Naphthalenes + Fluorenes + Phenanthrenes + Dibenzothiophenes})}{\text{Phenanthrenes + Dibenzothiophenes}}.$$

$$ALK/ISO = \frac{(\Sigma \text{ alkanes; } C_{14}-C_{18})}{(\Sigma \text{ 5 isoprenoids; in n-}C_{13} \text{ boiling range})}.$$

PRIS = pristane

PHY = phytane

TABLE 1-4

INTERFACIAL TENSION OF CRUDE OIL AND OIL/DISPERSANT MIXTURES
VERSUS STANDARD SEAWATER (35 o/oo) (dynes/cm)

	AT -5°C	AT 0°C	AT +5°C
Lagomedio crude	ND[a]	16.7	19.8
Lagomedio crude:Corexit 9527 (10:1)	1.7	1.3	3.4
Lagomedio crude:Corexit 9527 (1:1)	1.3	1.3	2.0

[a]Not determined.

TABLE 1-5

DENSITY OF CRUDE OIL AND OIL/DISPERSANT MIXTURES (g/cm^3)

	AT -5*C	AT 0"C	AT +5°C
Lagomedio crude	0.8990	0.8958	0.8923
Lagomedio crude:Corexit 9527 (10:1)	0.9118	0.9082	0.9045
Lagomedio crude:Corexit 9527 (1:1)	0.9621	0.9586	0.9551

TABLE 1-6

ABSOLUTE VISCOSITY OF CRUDE OIL AND OIL/DISPERSANT MIXTURES
(centistokes)

	AT -5°C	AT 0°C	AT +5°C
Lagomedio crude	Note[a]	Note[a]	154.1
Lagomedio crude:Corexit 9527 (10:1)	Notea	Notea	120.0
Lagomedio crude:Corexit 9527 (1:1)	218.0	144.6	100.3

[a]The samples appeared to precipitate waxy components at 0" C and -5° C. These prevented determination of the viscosity of the sample by clogging the orifice of the viscometer. The viscosities determined in the second section of the reverse flow viscometers used for the determinations were invariably higher than those determined in the first section.

Viscosity (centistokes)

At 0° C		At -5° c	
1st Section	2nd Section	1st Section	2nd Section
1,420	2,640	1,629	3,351
880	1,288	9,801	20,960

hydrocarbons (mainly phenanthrene, methyl phenan-threnes and perylene) were quantified as well. Their sources are global and/or local atmospheric transport of PAH from combustion of fossil fuels and in situ geochemical diagenesis.

4. Tissue hydrocarbon components are, for the most part, of biogenic origin although very low levels of some aromatic hydrocarbons can be detected (1-10 ppb) .

Details of baseline and oil characterization studies can be found in Boehm 1981a.

SECTION TWO

SECTION TWO

SAMPLING AND ANALYTICAL METHODOLOGY

2.1 Sampling

Samples of seawater, offshore sediments, beach sediments, benthic animals, and surface oil were collected from four experimental bays on Cape Hatt, Baffin Island, during August and September, 1981 (Figures 2.1, 2.2). Bay 11 was the site of the August 19 surface oil spill; Bay 9 was the site of the August 27 dispersed oil spill (Figure 2.2). Bays 10 and 7 were intended as control sites. However, Bay 10 received oil from the dispersed oil spill in Bay 9 making it a second test bay. A detailed description of the sampling techniques used appears in the first volume of this report (Green et al., 1982). A summary of the sampling design and methodology is presented here.

The generalized sampling design for each of the experimental bays was identical. Each bay was sampled three times during the summer field season: before any oil was spilled (pre-spill), one to three days after the oil spill (1st post-spill), and two to three weeks after the oil spill (2nd post-spill). The sampling grid was centered around two depth strata (Figure 2.3) 150 meters long running parallel to shore along the 3-meter and 7-meter depth contours (Figure 2.3). Animals and sediments for chemical analysis were collected from the five "Tissue plots" located along each depth stratum. Sediment samples were also collected from the biology stations located 1-3 meters shoreward from the tissue plots along each depth stratum and at two stations located at the 10-meter depth directly offshore from the ends of the 7-meter stratum ("Microbiology plot" stations). Water samples were collected at known reference points such
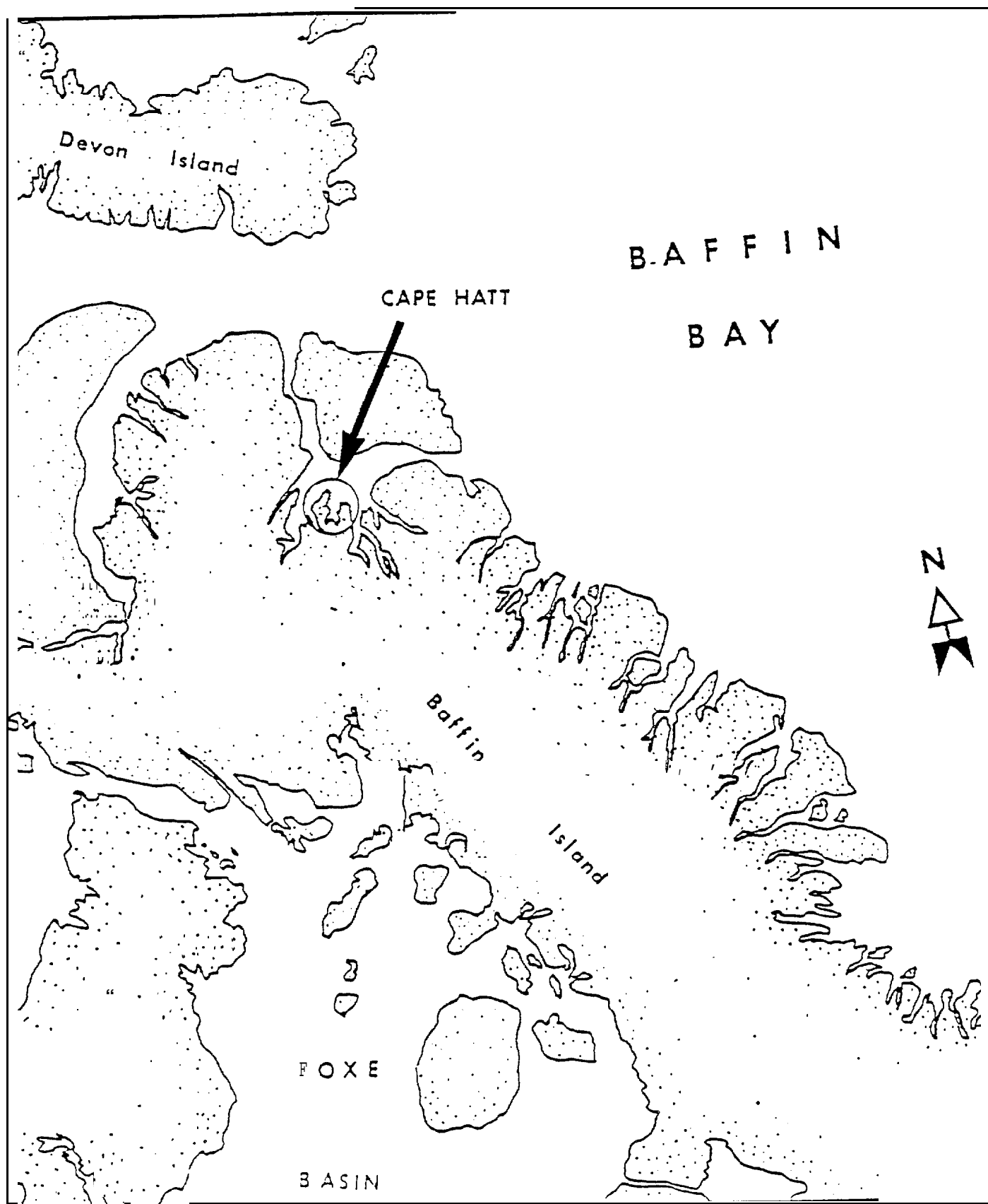
Figure 2.1. Location of Cape Hatt, Baffin Island.

"Z" Lagoon

Tukayat Lake

CAMP

AIR STRIP

Ragged Channel

110

102

101

108
109

107

104
105
103

106

14

13

12

11

10

9

7

CAPE HATT

Baffin Island
Northwest Territories
Lat. 72°30   Long. 79°50'

500   0   1000
Approx scale in metres
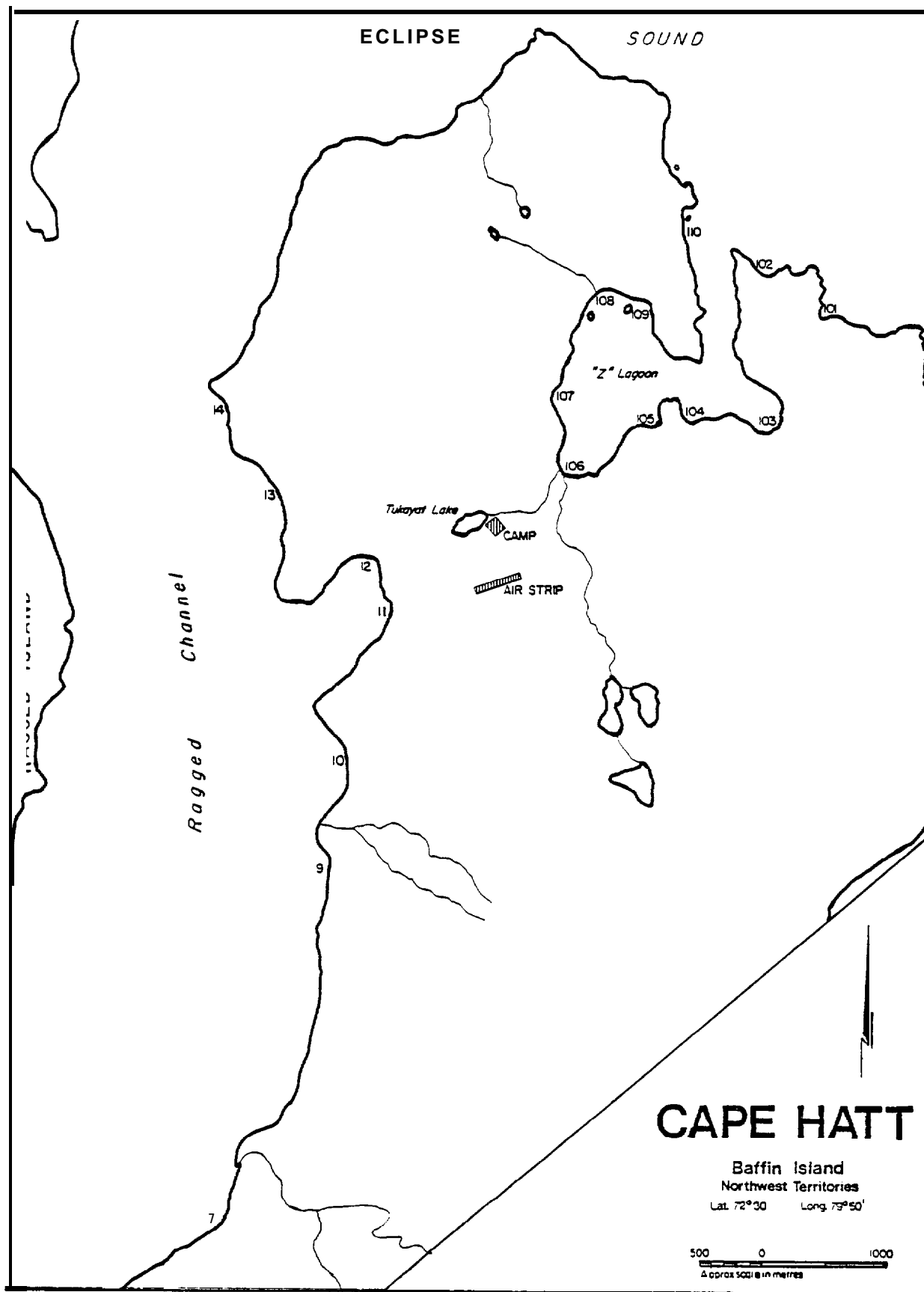
Figure 2.2. Detail of Test Bay Locations.
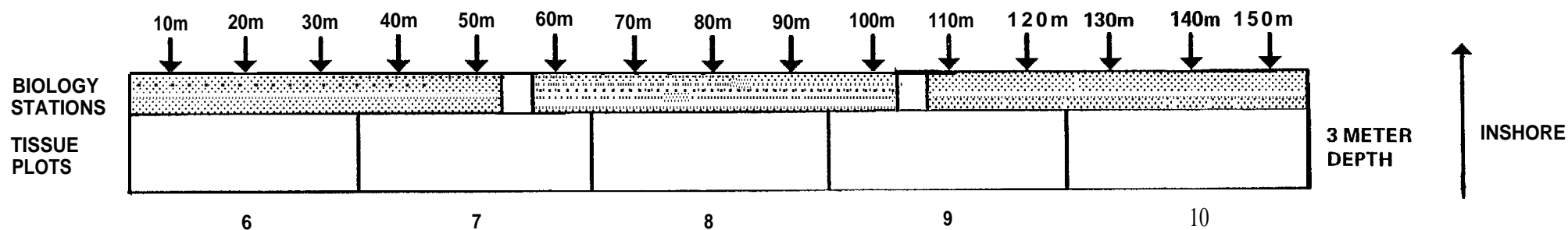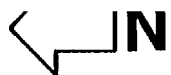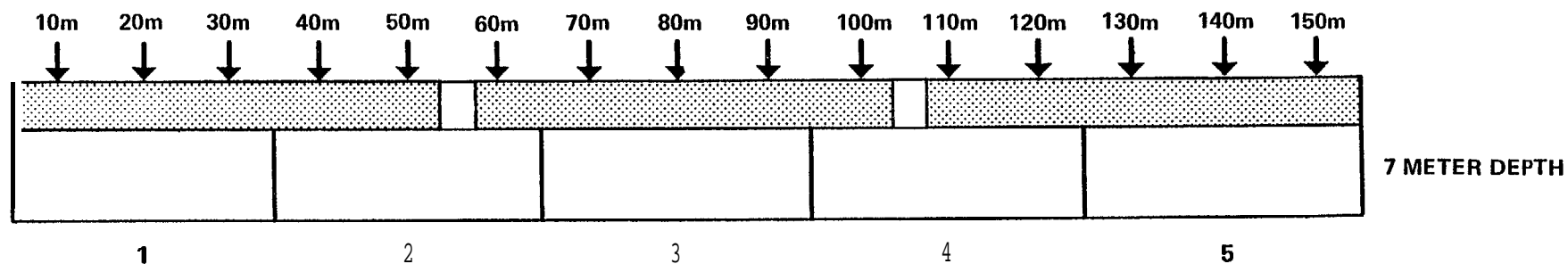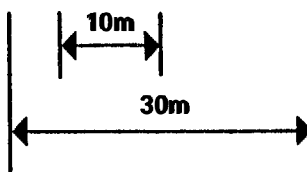
Figure 2.3. Station Designations- Used for Sediment Sampling (Biology Stations, Tissue Plots, Micro Plots) Tissue Sampling for Chemistry (Tissue Plots) and Sea Water Sampling (Baffin Queen Raft, Micro Stations).

as the buoys marking the microbiology plots and the Baffin
Queen anchor (located between Tissue Plot Stations 3 and 8),
from submersible pumps anchored at known locations, or at
various sites of opportunity.

2.1.1 Seawater Sampling

Seawater was collected from Bays 9, 10, 11 and 7 for
three types of analyses: (1) low-molecular-weight hydrocarbon
analysis, (2) high-molecular-weight hydrocarbon analysis
from 4 liter samples, and (3) high-molecular-weight hydrocarbon
analyses from large volume samples. Samples for low-molecular-
weight hydrocarbon analysis were collected from submersible
pumping systems constructed of nylon, polyethylene and
metal. Seawater was pumped directly into a 250-ml amber
glass bottle which contained mercuric chloride as a preserva-
tive. The bottle was sealed with a sheet of Teflon and a
crimp cap and stored at ambient temperatures (0-10° C) until
shipment. Once received at ERCO, these samples were stored
in a refrigerator at 4° C.

Samples for high-molecular-weight hydrocarbon analysis
(4 liter) were collected from either the submersible
pumping systems described above and located at the Baffin
Queen location in the center of the bay or along two transects
perpendicular to the shoreline from depths of ~3, 7 and 10
meters (i.e., bottom waters). Seawater pumped from these
locations was collected at two shoreline locations, SS1 and
SS2 (see Figure 2.4). In Bay 11, in addition to the Baffin
Queen, SS1, SS2 N-micro and S-micro locations, 3 liter (NBS
sampler) water samples were taken along the oil-containment
boom ("North, Mid and South Boom") in the bay. Note that in
Bay 11 the micro plots were outside of the boom while the
Baffin Queen Station was inside of the boom.
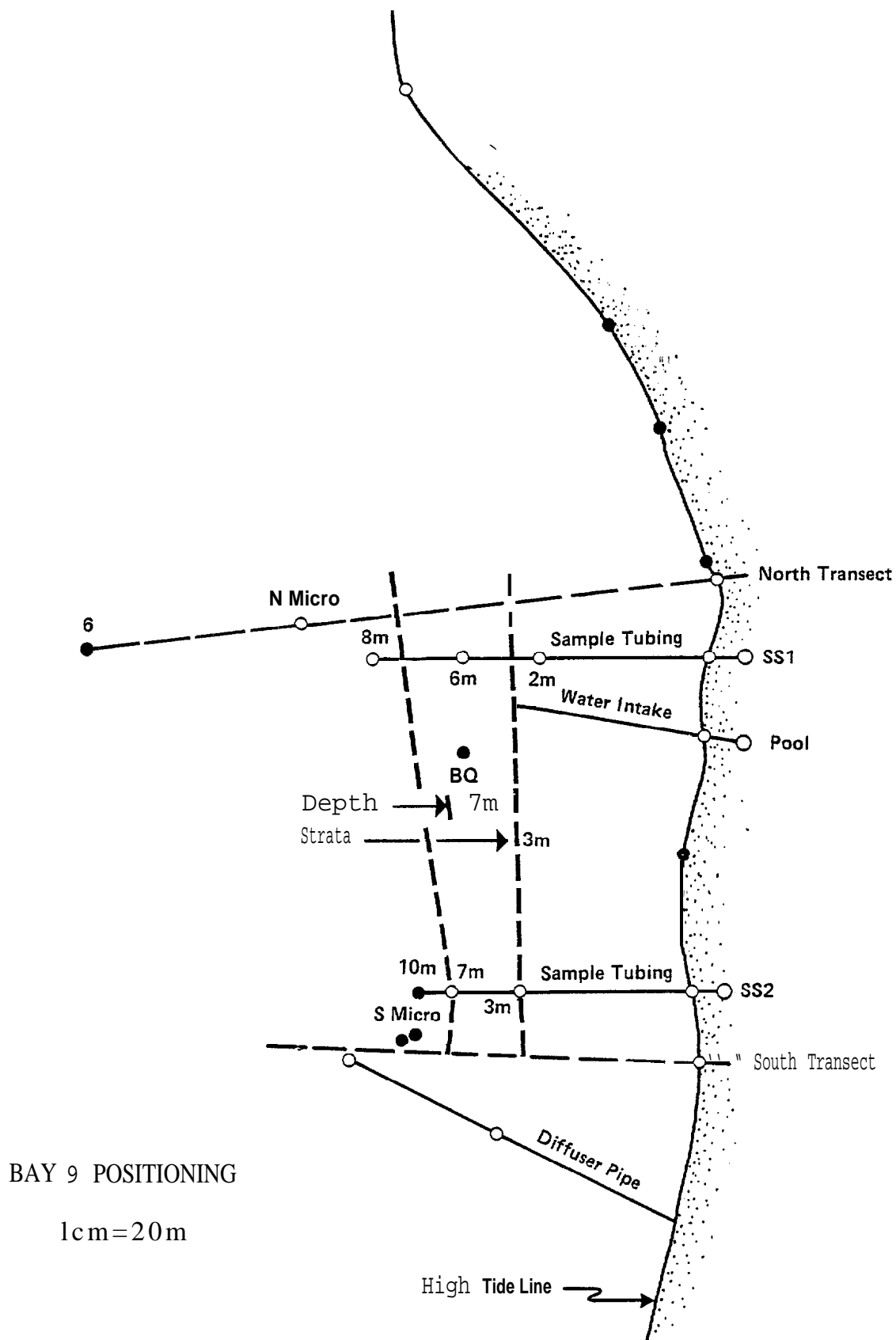
Figure 2.4. Location of Sampling Points within Experimental Bays (Bay 9).

A National Bureau of Standards (NBS) water sampler was used at the micro stations. A 4-liter solvent-rinsed glass bottle was filled with seawater, sealed with a sheet of Teflon and a screw cap, and stored at ambient temperatures until transported to the field laboratory (within 8 hours). At the field laboratory, the samples were preserved by adding 75 ml of Freon 113 to the bottle and then stored at room temperature until extraction.

Samples for large-volume high-molecular-weight hydrocarbon analysis were collected with an <u>in situ</u> filtration/adsorption sampler. The sampler consisted of a submersible pump, a 293-mm glass fiber filter held in a stainless steel holder, a series of polyurethane plugs in a glass cylinder held in a Teflon sleeve and a flow measurement device. The apparatus was deployed for a period of 4 to 12 hours during which 30 to 200 liters of seawater were pumped through the sampler. Particulate in the seawater were trapped on the filter which was simply folded, placed in an aluminum foil pouch and frozen. Dissolved organics were adsorbed to the polyurethane plugs in the glass cylinder which was sealed on each end with a sheet of Teflon and frozen.

2.1.2 Sediment Sampling

Sediments were collected from the beaches in Bay 9, Bay 11 and the countermeasures test area (shoreline study) and from the subtidal bottom in Bays 9, 10, 11 and 7 for high-molecular-weight hydrocarbon analysis. Beach sediment stations were located using transect markers established in Bay 9 and Bay 11 and from beach plot markers in the counter-measures test area. The samples from the 1980 and 1981 countermeasures plots (shoreline study in Z-lagoon) were taken from randomly predesignated subareas within a test

plot. Beach sediments from Bay 11 were sampled from three
stations (high-, mid- and low-tide marks) along each of two
transects (#4 and #6) on August 20, August 31 and September
9, which were 1, 12, and 21 days, respectively, following
the surface oil spill. Beach sediments from three transects
in Bay 9 were collected only once, on August 31 four days
after the dispersed oil spill. A summary of the sample
collection appears in Table 2-1.

At each station, beach material was scooped into a
solvent-rinsed glass jar with a stainless steel trowel.
Surface sediment was taken from the top 5 centimeters,
subsurface sediment from a depth of 10-15 cm. Care was
taken to ensure that the subsurface sample was not contami-
nated with surface sediment. The samples were transported
to the field laboratory and frozen.

Subtidal sediments (see Figure 2.3) were collected from
Bays 9, 10, 11 and 7 by using the same sampling design for
each bay. Three samplings (pre-spill, 1st post-spill and 2nd
post-spill) were conducted. During the pre-spill sampling,
surface sediment (0-2 cm) was collected from the tissue plot
stations (#1-IO) in Bays 9, 10, 11 and 7 (Table 2-2). Surface
floe from the sediment/water interface was collected at the
same stations in Bays 9, 10 and 11. Floe was not collected
from Bay 7. All pre-spill samplings were completed prior to
the surface oil discharge on August 19.

The first post-spill sampling of Bay 11 occurred on
August 21 two days following the surface oil spill. Bays 9, 10
and 7 were sampled on August 28, 29 and 31, respectively,
following the dispersed oil spill on August 27. Three samples
of surface sediment from each tissue plot station, one sample
of floe from each tissue plot station and 5 samples of
surface sediment spaced at 10-meter intervals within each

TABLE 2-1

SUMMARY OF BEACH SEDIMENT SAMPLING DATES

BAY	TRANSECT	BEACH FACE LOCATION	SAMPLING DEPTH	SAMPLING #1	#2	#3
11	4	High	Surface	Aug 20	Aug 31	Sep 9
		Mid	Surface	Aug 20	Aug 31	Sep 9
		Low	Surface	Aug 20	Aug 31	Sep 9
	6	High	Surface	Aug 20	Aug 31	Sep 9
		Mid	Surface	Aug 20	Aug 31	Sep 9
		Low	Surface	Aug 20	Aug 31	Sep 9
9	0	High	Surface	Aug 31		
		Mid	Surface	Aug 31		
		Low	Surface	Aug 31		
	1	High	Surface	Aug 31		
		High	Subsurface	Aug 31		
		Mid	Surface	Aug 31		
		Low	Surface	Aug 31		
	2	High	Surface	Aug 31		
		High	Subsurface	Aug 31		
		Mid	Surface	Aug 31		
		Low	Surface	Aug 31		

TABLE 2-2

SUMMARY OF OFFSHORE SEDIMENT SAMPLING DATES.

BAY	SAMPLING		
	PRE-SPILL	1st POST-SPILL	2nd POST-SPILL
Bay 9			
Floe (#1-10)[a]	Aug 16	Aug 28	Sep 10
Sediments (#1-10)	Aug 9-10	Aug 28	Sep 10
Sediments (Biology Stations)		Aug 28	Sep 10
Bay 10			
Floe (#1-10)	Aug 14	Aug 29	Sep 11
Sediments (#1-10)	Aug 14	Aug 29	Sep 11
Sediments (Biology Stations)		Aug 29	Sep 11
Bay 11			
Floe (#1-10)	Aug 12	Aug 21	Sep 8
Sediments (#1-10)	Aug 12	Aug 21	Sep 8
Sediments (Biology Stations)		Aug 21	Sep 8
Bay 7			
Floe (#1-10)	--	Aug 31	Sep 10
Sediments (#1-10)	Aug 17	Aug 31	Sep 10
Sediments (Biology Stations)		Aug 31	Sep 10

[a]#1-10 indicates tissue plot numbers.

biology station were collected from each bay (see Figure 2-3).
The second post-spill sampling was conducted similarly
in Bay 11 on September 8, in Bays 9 and 10 on September 10 and
in Bay 7 on September 11. Additional surface sediment samples
were collected from the microbiology plots (Hl-H8) at
weekly intervals on August 8, 14-18, 23, 30-31 and September
5, 12 and 18.

Divers collected surface sediment (0-2 cm) by scooping
a glass jar along the sediment surface. Unfilled jars were
taken through the water surface in a PVC tube whose ends
were capped with PVC screw caps and sealed with polyethylene
bags. Once below the surface the bags were cut, allowing
the tube to flood with seawater and become negatively
buoyant. Jars were dispensed from the bottom of the tube
and replaced at the top of the tube when filled with sediment.

Divers collected floe with a sampler that consisted of an
inverted polyethylene funnel (diameter = 20 cm), a length of
Tygon tubing (1 cm diameter x 1 m length), a submersible pump,
a metal diverter valve and a stainless steel filter holder
(142 mm diameter). The collection procedure was as follows.
A glass fiber filter (Gelman Type AE) was placed in the filter
holder, the apparatus was lowered over the side of an infla-
table boat and the pump was primed with clean water. With the
diverter valve in the "Waste" position, the pump was turned
on and lowered to the bottom. When positioned, the diver
placed the funnel on the sediment surface and turned the
diverter valve to the "Collect" position which directed the
seawater/floe slurry to the filter holder. The diver held
the funnel in position for 30 seconds at each of four loca-
tions, thereby collecting floe from a surface area of approxi-
mately 0.1 m^2.

Suspended sediments were collected in sediment traps
deployed by divers at easily found locations such as the end
of a transect or the **Baffin** Queen anchor.   The traps were
left in place for several days to two weeks.   Samples were
collected in all four bays at various time intervals
(Table 2-3) .

The trap, which consisted of a glass beaker inside a
PVC cylinder (11 cm diameter x 50 cm length) mounted on a
base, was capped and held vertically during deployment and
recovery operations.   When recovered, the water in the top
of the trap was drained through a bung.   The contents of the
beaker were poured into a glass jar and frozen.   Typically,
biological detritus and fine sediment were collected by the
sampler.

2.1.3 **Benthic Animal** Sampling

Benthic animals were collected from Bays 9, 10, 11,
and 7 during the **pre-spill,** 1st post-spill and 2nd post-spill
samplings.   Two collections, one handpicked and the other
airlifted, were performed in each bay.   **Mya truncata** (bivalve)
were hand collected from the tissue **plot** stations (#l-5)
near the 7-meter transect in Bays 9, 10, 11 and 7.   **Mya
truncata** were also collected from tissue plot stations
(#6-10) near the 3-meter transect in Bays 9 and 10 but were
not abundant enough at these stations in either Bay 7 or 11
to allow collection.   Six bivalves **(Macoma calcarea, Macoma
moesta,** Astarte borealis, Astarte **montagui, Nuculana** minuta
and **Serripes groenlandica)** were collected with an airlift
from the five tissue plot stations (#l-5) near the 7-meter
transect.   During the first post-spill sampling, additional
distressed Serripes from the sediment surface of Bays 9 and
10 were collected by hand.

Table 2-3

SUMMARY OF SEDIMENT TRAP
SAMPLE COLLECTION DATA

BAY	STATION	SAMPLING INTERVAL	DEPTH	DEPLOYMENT DATE	RETRIEVAL DATE	FIELD ID
11	BQ	O-3 days	3 m	18 Aug.	23 Aug.	PO05
	BQ	O-3 days	3 m	18 Aug.	23 Aug.	PO06
11	BQ	4-7 days	3 m	23 Aug.	27 Aug.	PO07
	BQ	4-7 days	3 m	23 Aug.	27 Aug.	PO08
9	H	Prespill	10 m	13 Aug.	18 Aug.	Pool
	H	Prespill	10 m	13 Aug.	18 Aug.	PO02
	1	0-3 days	7 m	27 Aug.	30 Aug.	PO09
	5	0-3 days	7 m	27 Aug.	30 Aug.	Polo
	10	0-3 days	3 m	27 Aug.	30 Aug.	P012
	5	4-7 days	7 m	1 Sep.	5 Sep.	P020
	6	4-7 days	3 m	1 Sep.	5 Sep.	P021
	10	4-7 days	3 m	1 Sep.	5 Sep.	P019
	1	7-21 days	7 m	5 Sep.	18 Sep.	P027
	6	7-21 days	3 m	5 Sep.	18 Sep.	P026
10	H	Prespill	10 m	14 Aug.	18 Aug.	PO03
	H	Prespill	10 m	14 Aug.	18 Aug.	PO04
	1	0-3 days	7 m	27 Aug.	30 Aug.	P013
	6	0-3 days	7 m	27 Aug.	30 Aug.	P014
	1	4-7 days	7 m	30 Aug.	5 Sep.	P023
	6	4-7 days	3 m	30 Aug.	5 Sep.	P024
	1	7-21 days	7 m	5 Sep.	18 Sep.	P029
	6	7-21 days	3 m	5 Sep.	18 Sep.	P028
7	1	0-7 days	7 m	27 Aug.	5 Sep.	P018
	6	0-7 days	3 m	27 Aug.	5 Sep.	P017

The collection schedule for the benthic animals is shown
in Table 2-4.

Divers picked **Mya** truncata using clean gloves. Animals
collected from individual stations were **placed** in **nylon** mesh
bags which were sealed in plastic bags underwater before
being carried through the water surface.   The contents of
the mesh bag were transferred to a plastic bag, labeled, and
transported to the field laboratory.   The animals were then
sorted by species, wrapped in aluminum foil, and frozen.

The airlift transferred animals, rocks and mud from the
sediment surface into a mesh bag at the opposite end of the
airlift.   The mesh bag was carried through the water surface
in a plastic bag and transported to the field laboratory.
The animals were picked from the agglomeration of debris,
sorted by species, wrapped in aluminum foil, and frozen.

2.2   Analytical Methods

The general analytical strategy for the chemical **assess-**
ment consisted of three levels (Figure 2.5).   In the first
level, samples were extracted and analyzed by ultraviolet
spectrofluorometry (UV/F) to measure the concentration of
petroleum.   Those samples either containing high levels of
petroleum or of interest due to sampling time and position
were carried through to the second level, fused silica glass
capillary gas chromatography with flame ionization detection
(GC^2).   This technique was used to quantify hydrocarbons,
to distinguish petroleum hydrocarbons from **biogenic** hydro-
carbons, and to evaluate the composition of petroleum.
Measurement of levels of individual aromatic hydrocarbons

TABLE 2-4

SUMMARY OF BENTHIC ANIMAL SAMPLING DATES

BAY	DEPTH STRATUM	SAMPLING TIME	PRESPILL	FIRST PRESPILL	SECOND PRESPILL
9	3m	Hand	Aug. 9	Aug. 29	Sep. 10
	7m	Hand	Aug. 7-9	Aug. 28,31[1]	Sep. 10
		Airlift	Aug. 8-9	Aug. 28[1]	Sep. 11
10	3m	Hand	Aug. 15	Aug. 29[2]	Sep. 11
	7m	Hand	Aug. 14	Aug. 28,30[2]	Sep. 11
		Airlift	Aug. 14	Sep. 1[2]	Sep. 11
11	7m	Hand	Aug. 12	Aug. 21	Sep. 11
		Airlift	Aug. 13	Aug. 21	Sep. 11
				Aug. 25	
7	7m	Hand	Aug. 17	Aug. 31[1]	Sep. 11
		Airlift	Aug. 17	Sep. 1-3	Sep. 11

[1]Serripes were airlifted from Bay 9 on August 28 and hand-picked on August 31.

[2]Serripes were airlifted from the 7m transect in Bay 10 on September 1 and hand-picked on August 30. Serripes were hand-picked from the 3m depth stratum on August 29.
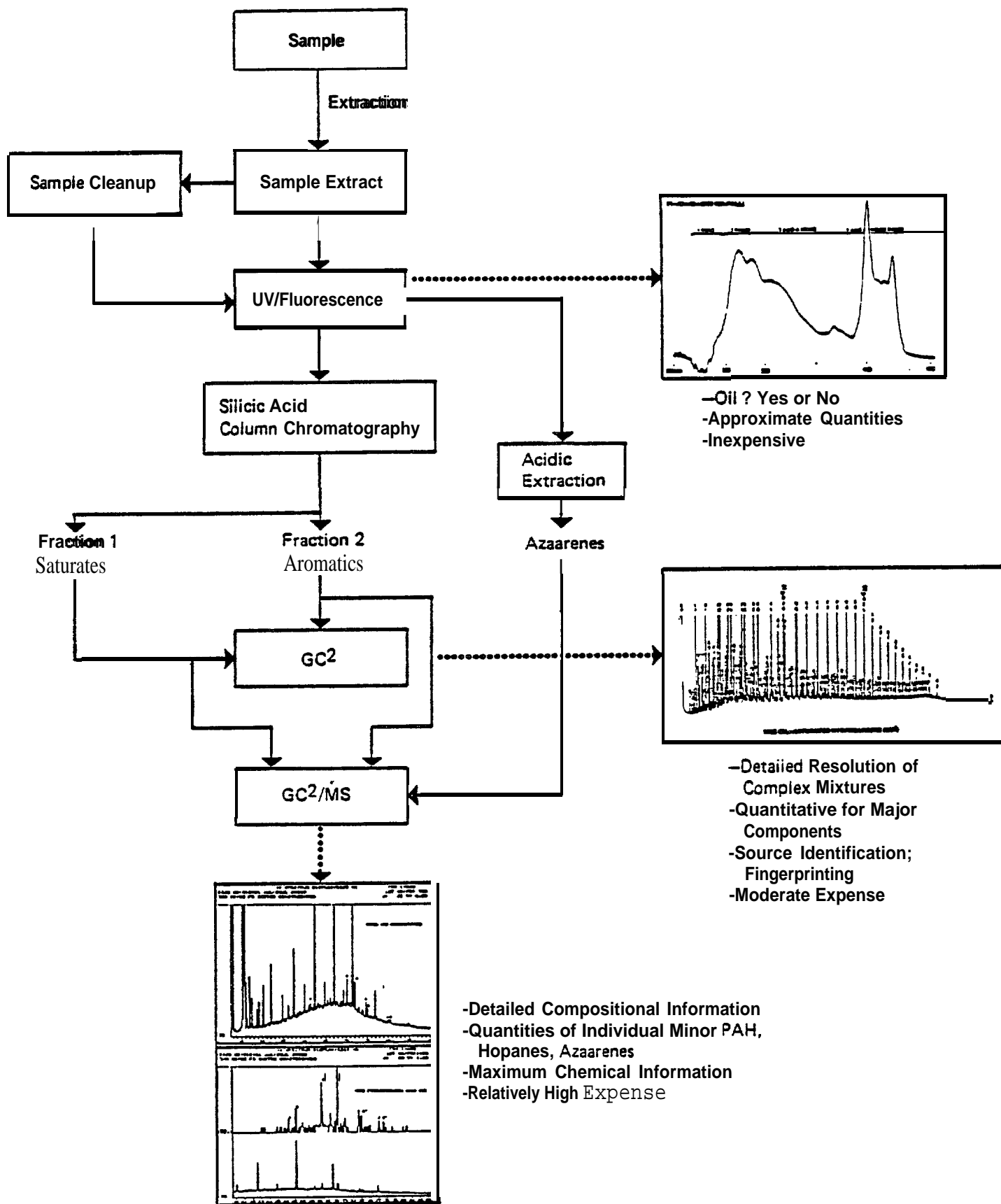
Figure 2.5. Schematic of Analytical Strategy.

was accomplished during the third phase when computer-assisted gas-chromatographic/mass spectrometry (GC^2/MS) was used.

Four types of samples (water, sediments, tissues, and oils), were analyzed within this study, each according to a slightly different analysis scheme. Each sample type required a unique initial processing/sample extraction protocol and followed its own analytical scheme (see Figure 1.2).

2.2.1 Water Sample Processing

Three types of water samples were analyzed: low molecular weight hydrocarbon samples, high molecular weight hydrocarbon samples (4 liters) and large-volume high molecular weight hydrocarbon samples. Each was analyzed by a unique set of analytical methodologies. None of the samples was screened by UV/fluorescence analysis; all were analyzed by GC^2, and a subset by GC^2/MS.

2.2.1.1 Low Molecular Weight Hydrocarbon Analysis

Water samples were analyzed for low molecular weight hydrocarbons (C_6 - C_{10}) by packed column gas chromatography/flame ionization detection using the method of Pojasek and Scott (1981). A 10 ml aliquot of water was dispensed with a pipet to a 40 ml glass vial containing 1 ml Hg metal. The vial was sealed with a teflon-faced silicone septum, inverted and heated at 90° C for 30 min in a water bath to allow the water and headspace to equilibrate. A 2 ml aliquot of the headspace was withdrawn through the septum via a 5 ml gas-tide syringe and immediately injected into the gas chromatography (Table 2-5). Peaks were identified by comparing retention times of peaks in the samples

TABLE 2-5

<u>PACKED COLUMN GAS CHROMATOGRAPHY/</u>
<u>FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS</u>

Instrument: Varian 3750 gas chromatography

Features: Varian Vista 401 data system

Inlet: Packed Column

Detector: Flame ionization

Column: 1/8" ID X 8' stainless steel packed with
                       10% 1,2,3 tris (2 cyanoethoxy) propane
                       on 1001 120 chromasorb P AW

Gases:

  Carrier: Helium 250 ml/min
  Detector: Air 300 ml/min
                       Hydrogen 30 ml/min

Temperatures:
  Injection port: 200° c
  Detector: 250° C
  Column oven: 50°-100° @ 10° C/rein

Daily calibration: Alkane/aromatic mixture

Quantification: External standard

with those of standard compounds. Quantification was
performed using the external standard method of quantifica-
tion. Response factors were calculated from analyses of
standards prepared in an identical fashion.

2.2.1.2 High Molecular Weight Hydrocarbon Analysis (4 liter)

Four-liter seawater samples were analyzed for high
molecular weight hydrocarbons by GC^2. The water was
processed in the field laboratory by adding 75 ml of Freon
113 to the glass sample bottle, shaking the bottle for
3 minutes on a paint shaker, and drawing off the Freon using
a screw-on teflon stopcock. The extraction was repeated two
additional times, and the three extracts were combined,
reduced in volume to 10 ml by rotary evaporation and trans-
ferred to a glass tube for shipment. Procedural blanks were
processed periodically to check for contamination during the
field processing.

When received at ERCO, the extracts were dried with
sodium sulfate, evaporated to <1 ml by rotary evaporation,
and displaced with hexane. Three micrograms of two internal
standards, androstane and o-terphenyl, were added to the
extract. An aliquot of the extract was weighed on a Cahn
Model 25 electrobalance to determine total extractable
organics. Those samples containing high levels of total
extractable were fractionated by silica gel/alumina column
chromatography (see Section 2.2.7) into saturated and unsatu-
rated/aromatic fractions which were analyzed by GC^2 (see
Section 2.2.8). Those samples containing low levels of total
extractable were analyzed directly by GC^2 without column
chromatography. Aromatic fractions and total extracts of
selected samples were analzyed by GC^2/MS (see Section 2.2.9).

2.2.1.3 High Molecular Weight Hydrocarbon Analysis
(Large Volume)

Each large volume water sample consisted of a glass fiber filter containing particulate organics and a poly- urethane plug containing dissolved organics, both of which were analyzed for high-molecular weight hydrocarbons by GC^2. The filters were processed by cutting them into small pieces which were placed into 250-ml Teflon jars. Three micrograms of two internal standards (androstane and o-terphenyl) and 100 ml of a mixture of dichloromethane and methanol (9:1) were added. The jars were shaken for four hours, and the solvent was decanted. The extraction was repeated with two additional portions of solvent, and the three extracts were combined, dried with sodium sulfate, reduced in volume to <1 ml by rotary evaporation and displaced with hexane. An aliquot of each of the extracts was weighed on a Cahn Model 25 electrobalance to determine total extract- able organics. The extracts were fractionated by silica gel/ alumina column chromatography (see Section 2.2.6) into saturated and unsaturated/aromatic fractions which were analyzed by GC^2 (see Section 2.2.8). Aromatic fractions of selected samples were analyzed by capillary GC^2/MS (see Section 2.2.9).

The plugs were processed by extracting them in a Soxhlet extractor for 24 hours with methanol to remove water and then with dichloromethane:methanol (9:1) to extract organic compounds. All solvent extracts from a sample were combined in a one-liter separator funnel, the dicholoro- methane layer was drawn off, and the remaining water/methanol was extracted three times with 75 ml of dichloromethane. The dichloromethane extracts from a sample were combined, reduced in volume to <1 ml by rotary evaporation and displaced with hexane. An aliquot of each of the extracts was weighed

on a Cahn Model 25 **electrobalance** to determine total
extractable organ **ics.** The extracts were fractionated
by silica gel/alumina column chromatography (see Section
2.2.7) into saturated and unsaturated/aromatic fractions
which were analyzed by capillary GC^2 (see Section 2.2.8).
Aromatic fractions of selected samples were analyzed by
capillary GC^2/MS (see Section 2.2.9).

2.2.2 Sediment Sample Processing

Four types of sediment samples were collected and
analyzed: surface sediment samples (O-2 cm), sediment
floe samples, oiled beach sediments, and sediment trap
samples. Each was analyzed by a unique set of analytical
methodologies.

2.2.2.1 Surface Sediment Sample Analysis (O-2 cm)

Surface sediment samples were analyzed for high molecu-
lar weight hydrocarbons using both **UV/fluorescence (UV/F)**
and GC^2 techniques. Ten gram **subsamples** from the tissue
plots and microbiology stations were analyzed by UV/F
using the analytical method described below. Selected
samples from individual tissue plots and microbiology
stations were analyzed by GC^2 using an additional **subsample**
($\sim$100 g). Selected sediments collected from the benthic
transects (see Figure 2.3 and Figure 2.6) were analyzed by
UV/F using a 10 g **subsample.** Extracts from a given bay,
sampling time, transect, and nest (see Figure 2.6) (5
stations/nest) were combined, fractionated by silica gel/
alumina column chromatography (see Section 2.2.7) into
saturated and unsaturated/ aromatic fractions which were
analyzed by GC^2 (see Section 2.2.8).

X Denotes that the Sample
was Analyzed by UV/F

* Denotes a Pooled Sample
Extract that was Analyzed
by GC2

—Denotes that Sample was
not Analyzed by UV/F

N

STATION 1   STATION 2   STATION 3

| x | x | x | X | — | x | x | x | X | — | — | x | x | x | x |
| 10m | 20m | 30m | 40m | 50m | 60m | 70m | 80m | 90m | 100m | 110m | 120m | 130m | 140m | 150m |

3 and 7 Meter
Depths
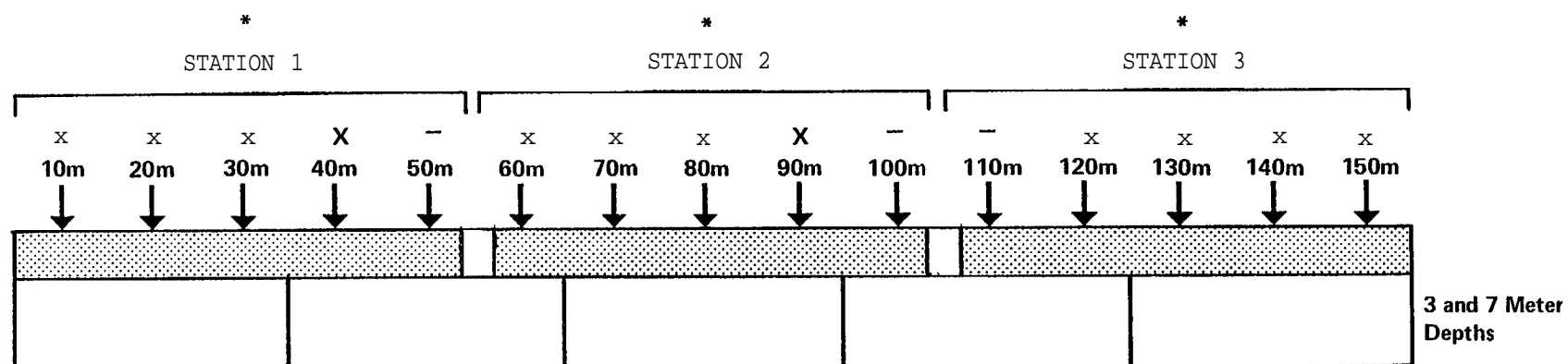
Figure 2.6. Illustration of the Selection of Individual Sampling Points & the Pooling
of Sediment Samples from "Biology Stations".

The extraction method for the UV/F analyses of sediment samples was a modified version of the GC^2 method described below. Approximately 10 g of wet sediment was weighed into a 50 ml glass centrifuge tube with a Teflon closure. The sediment was dried by extracting 3 times with 15 ml of methanol. The dry sediment was then extracted four times with 20 ml of dichloromethane:methanol(9:1) by shaking for 10 minutes on an orbital shaker for each extraction. Al 1 solvent extracts were transferred to a 250 ml separator funnel containing 50 ml of water (Millipore RO) and acidified to a pH of 2 with hydrochloric acid. The dichloromethane layer was drawn off and the aqueous methanol phase was extracted three times with 15 ml of dichloromethane. The dichloromethane extracts were combined, reduced in volume to < 1 ml by rotary evaporation and displaced with hexane.

Polar compounds which interfered with the UV/F analysis were removed from the extract by alumina column chromatography. The procedure was based on the methodology of Georlitz and Law (1974) and is summarized below. The total extract was charged to a chromatography column (9 mm ID) containing 6.5 g of a 7.5% water deactivated alumina that was wet-packed in hexane and prepared by eluting with 30 ml of hexane. The column was eluted with 25 ml of hexane to isolate the saturated, unsaturated, and aromatic compounds. The hexane fraction was concentrated by rotary evaporation, displaced with cyclohexane and analyzed by UV/F (see Section 2.2.5).

The extraction method for the capillary GC^2 analysis (Figure 2-7) of sediment samples was based on methods of Brown et al. (1979) and Boehm et al. (1981). Approximately 100 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 75 ml of methanol. Five micrograms of two internal standards, androstane and o-terphenyl were added to the sediment. The dry sediment

```
                    ┌──────────────────────┐
                    │   Sediment Sample    │
                    └──────────────────────┘
                              │
        1) Place 100 g Subsample in Teflon Jar
        2) Extract 3x with CH30H (Shake 0.5 Hr Each Extraction}
        3) Add I.S. (f1 & f2)
        4) Extract 3 x with CH2Cl2/CH3OH (9:1)
           (Shake 4 Hr at Room Temperature for Each Extraction)
        5) Combine Extracts with 100 ml Water
```

Sediment	**Combined Extracts**

Weigh
Discard

6) Remove CH_2Cl_2 Layer
7) Extract Aqueous Phase 3 x with CH_2Cl_2
8) Combine CH2C12 Extracts
9) Concentrate to < 1 ml
10) Displace with CH30H

Concentrated Extract

11) Transfer to 50 ml Tube
12) Add 15 ml CH_3OH,15 ml 10N KOH
13) Heat at 800C for 4 Hr to Saponify
14) Extract 3 x with Hexane
15) Concentrate
16) Weigh Aliquot of Extract

Saponify Extract

Silica Gel Column Chromatography

Hexane (f1)   Hexane/Meth ylene
                                    Chloride (f2)
(Weigh Aliquot)
                                    (Weigh Aliquot)

Saturated Hydrocarbons	Aromatic Hydrocarbons

| GC^2/FID | GC^2/FID |

| GC^2/MS |

Figure 2.7. Analytical Scheme for Hydrocarbon Analysis of Sediment Samples (GC^2/FID Analysis).

was then extracted three times with 100 ml of **dichloromethane:**
methanol (9:1) by shaking on a platform shaker for a minimum
of 4 hours for each extraction.   All solvent extracts were
transferred into a 1-liter separator funnel containing
100 ml of water (**millipore** RO) and acidified to a **pH** of
2 with hydrochloric acid.   The dichloromethane layer was
drawn off and the aqueous methanol phase was extracted
3 times with 50 ml of dichloromethane.   The **dichloromethane**
extracts from a sample were **combined,** reduced in volume to
<1 ml by rotary evaporation and displaced with methanol.
The extract was transferred to a 50 ml glass tube containing
10 ml of methanol and 4 ml of 10N aqueous KOH, sealed with
a Teflon cap and heated at 80° C for 4 hours to saponify
interfering polar compounds.   The mixture was cooled then
extracted 3 times with 15 ml of hexane.   The combined hexane
extracts were dried over sodium sulfate and concentrated
by rotary evaporation to approximately 1 ml.   An **aliquot** of
the extract was weighed on a Cahn Model 25 **electrobalance** to
determine total extractable **organics.**   The extracts were
fractionated by silica **gel/alumina** column chromatography
(see Section 2.2.7) into saturated and unsaturated aromatic
fractions which were analyzed by GC2 (see Section 2.2.1).
Aromatic fractions of selected samples were analyzed by
capillary GC^2/MS (see Section 2.2.9).

2.2.2.2 <u>Surface Floe Analysis</u>

Surface floe samples were analyzed for high molecular
weight hydrocarbons using both UV/F and GC2 techniques.
The glass fiber filters containing the floe were extracted
with dichloromethane:methanol (9:1) using the techniques
described for the large volume water sample filters in
Section 2.2.1.3.   The total extracts were freed of polar
compounds which interfere with the UV/F by alumina column

chromatography as described for surface sediments in Section
2.2.2.1.   All samples were analyzed by UV/F (Section 2.2.5),
and selected samples were fractionated by silica gel/alumina
column chromatography (Section 2.2.7) into saturated and
unsaturated aromatic fractions which were analyzed by GC^2
(Section 2.2.8).   Selected aromatic fractions were analyzed
by GC/MS (Section 2.2.9).

2.2.2.3 Oiled Beach Sediment Analysis

Oiled beach sediments were analyzed for high molecular
weight hydrocarbons using only GC^2 techniques.   The
analytical methodology was, with one exception, the same
as that described for GC^2 analysis of surface sediments in
Section 2.2.2.1.   The sediments contained small amounts of
water and were not dried with methanol prior to extracting
them with dichloromethane:methanol (9:1).   The total extracts
were fractionated by silica gel/alumina column chromatography
(Section 2.2.6) into saturated an unsaturated aromatic
fractions which were analyzed by capillary GC^2 (Section
2.2.7).   Aromatic fractions of selected samples were analyzed
by GC^2 (Section 2.2.8).

2.2.2.4 Sediment Trap Analysis

Sediment trap samples were analyzed for high-molecular
weight hydrocarbons using only GC^2 techniques.   The sediment/
water slurry (125 ml) was thawed, poured into a 250-ml separa-
tory funnel and extracted three times with 50 ml of dichloro-
methane.   Three micrograms of two internal standards, androstane
and o-terphenyl; were added to the extract which was dried
with sodium sulfate, reduced in volume to <1 ml and displaced
with hexane.   An aliquot of the extract was weighed on a Cahn

Model 25 electrobalance to determine total extractable organics. Those samples collected during the first week after the experimental spills were fractionated by silica gel/alumina column chromatography (Section 2.2.7) into saturated and unsaturated aromatic fractions which were analyzed by GC^2 (Section 2.2.8). Those samples collected during the second week after the spills were directly analyzed by GC^2 (Section 2.2.8).

2.2.3 Benthic Animal Tissue Processing

Five species of benthic bivalves were analyzed by ERCO: Mya truncata, Serripes groenlandica, Macoma calcarea, Nuculana minuta and Astarte borealis. Two other species, Strongylocentrotus droebachiensis (sea urchin) and Pectinaria (polychaete) were analyzed by Canadian Wildlife Service, and two additional bivalves species, Macoma moesta and Astarte montagui, remain unanalyzed and stored at ERCO. Samples from individual tissue plot stations were analyzed by UV/F. Subsequently, extracts from all five tissue plot stations from a given stratum, bay and sampling time were combined and analyzed by GC^2.

The extraction and analytical procedure (Figure 2.8) was based closely on that of Warner (1976) as revised by Boehm et al. (1982b). Clam tissues (guts, muscle, gills) were removed from the shells with solvent-rinsed utensils. Samples with more than 10 grams wet weight tissue were homogenized with a Vitris tissue homogenizer, and a 10 g aliquot **was taken** for analysis. Otherwise, the entire sample was homogenized. A small aliquot of the tissue homogenate was taken for wet weight/ dry weight determination. Tissue was digested overnight with a 5 N **aqueous potassium** hydroxide and methanol solution, and extracted with hexane.

```
                    ┌─────────────────────────┐
                    │                         │
                    │      Tissue Sample      │
                    │                         │
                    └─────────────────────────┘
                              │ 1 ) Homogenize
                              │ 2) Add to Teflon Jar
                              │ 3) Add Internal Standards
                              │ 4) 5N KOH (aq)
                              │ 5) Flush Jar with N2
                              │ 6) Seal
                              │ 7) Digest Overnight at Room Temperature with Shaking
                    ┌─────────────────────────┐
                    │                         │
                    │        Digestate        │
                    │                         │
                    └─────────────────────────┘
                              │ 8) Transfer to Separator Funnel
                              │ 9) Add Saturated NaCl
                              │ 10) Extract 5 Times with Hexane
                              │ 11 ) Concentrate
                              │ 12) Dry Over Na2S04
                    ┌─────────────────────────┐
                    │  Combined Hexane Extracts│
                    └─────────────────────────┘
                              │ 13) Alumina Column
                         f0   │     Chromatography (Hexane)
                    ┌─────────────────────────┐
                    │  Saturated and Aromatic │
                    │  Hydrocarbons           │
                    └─────────────────────────┘
                              │
                    ┌─────────────────────────┐
                    │  UV/Fluorescence Analysis│
                    └─────────────────────────┘
                              │
                    ┌─────────────────────────┐
                    │  Select Sample; Pool     │
                    │  Stations on a Transect  │
                    └─────────────────────────┘
                              │ Silica Gel Column Chromatography
           Hexane (f1)                    Hexane: MeCl2 (f2)
           (Weigh)                        (Weigh)
        ┌──────────────┐              ┌──────────────┐
        │ saturated    │              │ Aromatic     │
        │ Hydrocarbons │              │ Hydrocarbons │
        └──────────────┘              └──────────────┘
               │                             │
        ┌──────────────┐              ┌──────────────┐
        │    GC2       │              │    GC2       │
        └──────────────┘              └──────────────┘
                                             │
                                      ┌──────────────┐
                                      │   GC2/MS     │
                                      └──────────────┘
```
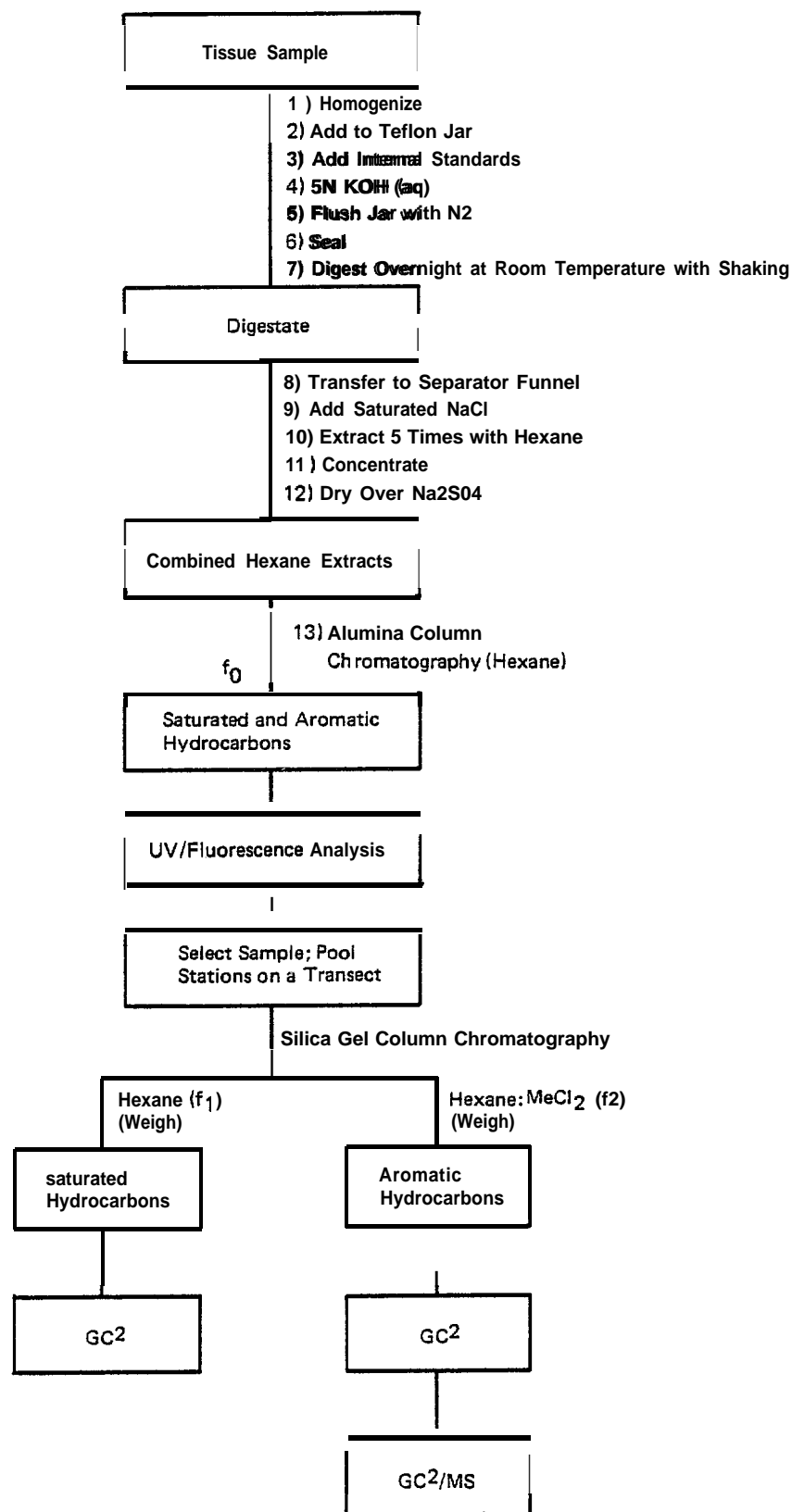
Figure 2.8. Analytical Scheme for Hydrocarbon Analysis of Tissue Samples
(from Warner, 1976; Boehm et al., 1982a).

Hexane extracts were combined, dried with sodium sulfate and
concentrated to 0.5 ml by rotary evaporation. Polar and
biogenic compounds which interfered with the UV/F analysis
were removed from the extract by aluminia column chroma-
tography. One of two sizes of columns, one containing 6.5 g
and the other containing 25 g of 7.5% water deactivated
alumina, were used depending on the amount of tissue. The
column was eluted with 25 ml or 75 ml of hexane, respectively,
to isolate the saturated, unsaturated and aromatic compounds.
The fraction was concentrated and transferred into cyclo-
hexane for UV/F analysis (Section 2.2.5).

After UV/F analysis, one half of each extract from the
tissue plot stations on each stratum (Stations 6-10 on the
3 m stratum and Stations 1-5 on the 7 m stratum) were combined,
concentrated by rotary evaporation and displaced with hexane.
The pooled extracts were fractionated by silica gel/alumina
column chromatography (Section 2.2.7) into saturated and
unsaturated/aromatic fractions which were analyzed by GC2
(Section 2.2.8). Selected extracts from individual tissue
plot stations were similarly fractionated and analyzed
by GC2. Aromatic fractions from selected samples were
analyzed by GC^2/MS (Section 2.2.9).

2.2.4 Oil Sample Processing

Two types of oil samples were collected during the BIOS
experiment: neat oils collected from the discharge pool and
oil drums and floating oil collected from the seawater
surface in the experimental bays. A weighed quantity of
the neat oils (∿20mg) and 20 µg of two internal standards
androstane and o-terphenyl was simply diluted with hexane,
and fractionated by silica gel/alumina column chromatography
(Section 2.2.7) into saturated and unsaturated aromatic

fractions which were analyzed by GC^2 (Section 2.2.7). The
floating oil/water mixtures were thawed, poured into a
250-ml separator funnel and extracted three times with 50
ml of **dichloromethane.** The extract **was** dried with sodium
sulfate concentrated by rotary evaporation and displaced
with hexane. An **aliquot** of the extract was weighed on a
Cahn Model 25 **electrobalance** to determine total extractable.
An **aliquot** containing approximately 20 mg of oil and 20 **μg**
each of two internal standards, androstane and **o-terphenyl,**
was fractionated and analyzed by GC^2 as described above
for the neat oils.

2.2.5 UV/F Analysis

The synchronous excitation/emission technique has been
widely employed in recent years to examine the detailed
fluorescent properties of environmental samples. The
technique is based on the methods of Wakeham (1977) and
Gordon and Keizer (1974). A measured **aliquot** of the sample
extract was dissolved in a known volume of **cyclohexane.** The
intensity of the fluorescence emission was measured from
250 to 500 nm while synchronously scanning the excitation
monochromes at a wavelength 25 nm less than the wavelength
of the emission **monochrommeter.** Analytical conditions are
shown in Table 2-6. This technique measures aromatic
hydrocarbons with a **two-** to five-ring aromatic structure
(Lloyd, 1971). The extract was repeatedly diluted by 50%
and reanalyzed until a comparison of two consecutive dilutions
indicated that the analysis was done within the linear range
of fluorescence response.

The intensity of the fluorescence spectra was measured
at 355 nm (or the nearest spectral maxima) which corresponded
to a peak maximum present in a Lagomedio Bay 11 reference

TABLE 2-6

UV SPECTROFLUOROMETRY ANALYTICAL CONDITIONS

Instrument:	Farrand Mark I **spectrofluorometer**
Features:	Corrected excitation Corrected emission
Slits:	
Excitation: Emission:	2.5 nm 5.0 nm
Scan speed:	50 **nm/min**
Cell:	10 mm quartz
Monochrometers :	<u>Synchronous</u>
Excitation: Emission:	225-475 nm 250-500 nm
Daily calibration:	Bay 11 Lagomedio oil
Quantification:	External standard

oil sample. The fluorescence spectra were converted to
relative concentration units by comparing the peak height at
each wavelength to that of the Bay 11 oil standard curve.

2.2.6 Variability in UV/F Measurements - Tissues

Triplicates taken from within a tissue plot station
(one tissue sample divided into 3 x 10 g each, and then
analyzed individually) were analyzed to measure the varia-
bility in the analytical method, from extraction of tissue
through UV/F measurements. The arithmetic means and stand-
ard deviations were as follows ($\mu g/g$ DW): 0.67 ± 0.12
(18%), Mya, Bay 10, prespill 21.2 ± 0.5 (23%), Astarte, Bay
11, first postspill; 111 ± 3.3 (3%), Mya, Bay 10, second
postspill 296 ± 30 (10%), Serripes, Bay 10, first postspill;
and 559 ± 119 (21%), Serripes, Bay 9, first postspill.

2.2.7 Fractionation

Those sediment, tissue, and water samples chosen for
GC^2 analyses and all of the oil samples were fractionated
by silica gel/alumina column chromatography prior to fused
silica capillary gas chromatography. Column chromatography
isolated the saturated and aromatic hydrocarbons from the
total extract, thereby facilitating the identification and
quantification of individual hydrocarbon compounds which
were present in the sample extract. The procedure was that
of Boehm et al. (1982b) and is summarized below.

The total extract was charged to a 100% activated
silica gel/5 percent deactivated alumina/activated copper
(11 g, 1 g, 2 g) chromatography column that was wet-packed
in dichloromethane and prepared by eluting with 30 ml each
of dichloromethane and hexane. The column was eluted with

18 ml of hexane followed by 21 ml of hexane:dichloromethane (1:1) to isolate the saturated (f_1) and unsaturated (f2) hydrocarbons, respectively. After concentrating each fraction by rotary evaporation, the total gravimetric concentration was determined by weighing a measured aliquot on a Cahn Model 25 electrobalance.

2.2.8 GC^2 Analysis

GC^2 analysis served to identify and quantify the petroleum hydrocarbon compounds present in the sample. The relative concentrations of individual compounds identified the composition of oil present, and the absolute concentrations served as a measure of the amount of oil present. The concentrations of certain compounds were also used to calculate indicator ratios that reveal the type of hydrocarbons present, i.e., biogenic or petroleum, and the weathering age of the petroleum.

Each fraction was analyzed by fused silica capillary gas chromatography on a Hewlett Packard 5840 or 5880 gas chromatography equipped with a splitless injection port and a flame ionization detector. Wall coated open tubular (WCOT) fused silica columns (0.25 mm x 30 m, J&W Scientific) coated with SE30 and SE52 stationary phases were used to analyze, respectively, the f_1 and f2 fractions from the column chromatography. The instrumental conditions are listed in Table 2-7. Compounds were identified by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane for the f_1, o-terphenyl for the f2). The total concentrations of saturated and

TABLE 2-7

FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/
FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS

Instrument: Hewlett Packard 5840 or 5880 gas
                      chromatography

Features: Split/splitless capillary inlet system
                      Microprocessor-controlled functions

Inlet: Splitless

Detector: Flame ionization

Column:

  f_1:   0.25 mm I.D. x 30 m
                        SE30 fused silica (J&W Scientific)

  f_2:   0.25 mm I.D. x 30 m
                        SE 52 fused silica (J&W) Scientific)

Gases:

  Carrier: Helium 2 ml/min
  Make-up: Helium 30 ml/min
  Detector: Air 300 ml/min (500 ml/min for 5880)

Temperatures:
  Injection port: 250° C
  Detector: 300° c
  Column oven: 40°-2900 @ 3° C/rein

Daily calibration: Alkane/aromatic mixture

Quantification: Internal standard (F_1 androstane,
                      f2 o-terphenyl)

aromatic hydrocarbons were determined by planimetering the unresolved area, converting it to integrator area units, adding it to the total resolved integrated area, and calculating a concentration using the internal standard method.

The analytical outputs from the GC2 analysis are listed in Tables 2-8 and 2-9. The concentrations of **n-alkanes** and isoprenoids were reported on a dry weight basis. From these concentrations a series of key diagnostic parameters were calculated. These ratios are useful in establishing the composition of the oil, the contribution of biogenic hydrocarbons, and the degree that the oil was weathered.

2.2.9 Gas Chromatography/Mass Spectrometry (GC^2/MS)

Selected samples found to contain petroleum by the GC^2 analyses were analyzed by **GC^2/MS** to measure the concentration of aromatic hydrocarbons **in** the samples. The concentrations of a series of **polynuclear** aromatic hydrocarbons, in particular the **alkylated** phenanthrenes and dibenzothiophenes, serve as a fingerprint of weathered petroleum.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography (see Section 2.2.6) was analyzed for **polynuclear** aromatic hydrocarbons by **GC^2/MS**. An **aliquot** of the fraction was analyzed using a Finnegan 4530 instrument equipped with a 0.25 mm x 30 m SE52 fused silica capillary column (J&W Scientific), which was threaded directly into the ion source. Instrumental conditions are listed in Table 2-10.

Selected ion searches were used to obtain ion **chromato-**grams for aromatic compounds with known retention indices and suspected to be present in the samples. If necessary, the mass spectrum and retention time of an identified

TABLE 2-8

COMPOUNDS QUANTIFIED BY FUSED SILICA
CAPILLARY GAS CHROMATOGRAPHY

COMPOUND	ANALYTICAL TECHNIQUE	USE
Saturated hydrocarbons		
n-alkanes ($n-C_{10}$ to $n-C_{34}$)	Capillary GC	Weathering and source indicators, especially when ratios are derived
Isoprenoids (farnesane, pristane, phytane, 1650, 1380)	Capillary GC	Weathering indicator (marker compounds as a group in lightly weathered samples)

TABLE 2-9

EXPLANATION OF PETROLEUM WEATHERING RATIOS

The Biodegradation Ratio (Alkane/Isoprenoid)

$$ALK/ISO_{14-18} = \frac{[1400] + [1500] + [1600] + [1700] + [1800]}{[1380] + [1470] + [1650] + [1708] + [1810]}$$

The **ALK/ISO** ratio approaches O as the **n-alkanes** are depleted.

The Saturated Hydrocarbon Weathering Ratio (SHWR)

$$SWHR = \frac{[\text{sum of } \mathbf{n\text{-}alkanes} \text{ from } \mathbf{n\text{-}C_{10}} \text{ to } \mathbf{n\text{-}C_{25}}]}{[\text{sum of } \mathbf{n\text{-}alkanes} \text{ from } \mathbf{n\text{-}C_{17}} \text{ to } \mathbf{n\text{-}C_{25}}]}$$

The SWHR approaches 1.0 as low-boiling saturated hydrocarbons ($n\text{-}C_{10}$ to $n\text{-}C_{17}$) are lost by evaporation.

The Aromatic Weathering Ratio (**AWR**)

$$AWR = \frac{\mathbf{Alkyl} \text{ benzenes} + \mathbf{naphthalenes} + \mathbf{fluorenes} + \text{phenanthrenes} + \text{dibenzothiophenes}}{\text{Total phenanthrenes} + \text{dibenzothiophenes}}$$

The AWR approaches 1.0 as low-boiling aromatics are lost by evaporation and/or dissolution.

TABLE 2-10

GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS

INSTRUMENT:	Finnegan 4530 gas chromatograph/mass spectrometer
FEATURES:	Data General Nova 3 data system with Incos data system Finnegan MAT 9610
INLET:	Splitless
DETECTOR:	Quadruple mass spectrometer
SCAN RATE:	450 amu/sec (45-450 amu)
IONIZATION VOLTAGE:	70 eV
COLUMN :	0.25 mm id. x 30 m SE52 fused silica (J&W Scientific)
INTERFACE:	Direct insertion of column into source
CARRIER GAS:	Helium 2 ml/min

TEMPERATURES :

INJECTION PORT:	270° C
SEPARATOR OVEN:	280″ C
SOURCE :	250° C
GC OVEN:	40-290° C, 10° C\min (temperature program)

DAILY CALIBRATION:	FC43, DFTPP and aromatic mixture
QUANTIFICATION:	Internal standard (o-terphenyl) (response factors)

peak was retrieved and compared with an authentic standard or to a mass spectrum library to aid in identification of the compound. An in-house probability-based computer matching system, the HP 7920 multi-disc system containing EPA/NIH probability-based mass spectral libraries, was utilized for this purpose.

Concentrations of the identified compounds were determined by measuring peak areas of the appropriate peaks in the selected ion chromatograms and relating them to that of the internal standard. Relative response factors for each component were calculated from analyses of analytical standards, if available, or were extrapolated. The compounds reported from the GC^2/MS analyses are listed in Table 2-11 and are presented in a series of Figures in the results section (e.g. Figure 3.21) with compound designations as in Table 2-11.

TABLE 2-11

GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYTICAL OUTPUTS

POLYNUCLEAR AROMATIC HYDROCARBONS

Alkyl benzenes (AB)

C3 to C_6 Benzenes (C_3AB-C_6AB)

Naphthalenes (N)
Naphthalene (C_0N)
2-Methyl naphthalene (C_1N)
l-Methyl naphthalene (C_1N)
c2 to C_4 Alkyl naphthalenes (C_2N-C_4N)

Biphenyl

Acenaphthene

Fluorene
C_1 to C3 Fluorenes

Phenanthrenes (P)
Phenanthrene (C_0P)
C_1 to C4 Phenanthrenes (C_1P) - C_4P)

Dibenzothiophenes (DBT)
Dibenzothiophene (C_0DBT)
C_1 to C3 Dibenzothiophene (C_1DBT-C_3DBT)

Fluoranthene

Pyrene
C_1 Pyrene

Benzo(a)anthracene

Chrysene
C_1 Chrysene

Benzofluoranthene

Benzo(a)pyrene
Benzo(e)pyrene

Perylene

SECTION THREE

SECTION THREE

RESULTS (NEARSHORE STUDY)

3.1 Water Column

    3.1.1 Oil on the Water's Surface and Spilled Oil
          Composition

    A series of thirteen oil samples taken from the Bay 9
or Bay 11 test areas was analyzed to determine the changing
molecular characteristics of the oil with time, due to the
collective processes of "weathering." The ALK/ISO and SHWR
ratios were used to monitor these changes as were the percent
saturates and percent aromatics parameters. Where GC^2/MS
was performed (3 samples) the AWR ratio was calculated.
Otherwise the concentration of the easily identified naphtha-
lene compounds was used as a weathering marker since the
quantity of these naphthalenes decreases as weathering
proceeds.

    The Table 3-1 results, all based on GC^2-derived
information, illustrates several interesting trends.
First, there are significant gross compositional differences
within both discharged oil pools. Note the percent saturates/
aromatics values of the two Bay 11 "pool" samples and the
two Bay 9 "diffuser pipe" samples. The ALK/ISO, SHWR and
AWR ratios are nearly identical for all discharged oil
initially. That oil weathers on the sea surface in Bay 11
is noted by the steadily decreasing SHWR values with time.
One day after the spillage the remaining surface oil has
lost 42% of its weatherable ($< n-C_{25}$) n-alkanes. The

Table 3.1. Surface oil compositional summary

				GROSS OIL COMPOSITION			SATURATED PARAMETERS		AROMATIC PARAMETERS			
SAMPLE			ID	PERCENT SATURATES	PERCENT AROMATICS	PERCENT RESIDUAL	ALK/ISO	SHWR	AWR[a]	N ($\mu g/mg$ oil)	C_1N ($\mu g/mg$ oil)	C_2 ($\mu g/mg$ oil)
BAY	LOCATION	DATE (TIME)										
11	Pool	8-19 (1600 hrs)	Q001	49.8	30.0	20.2	2.41	2.20	3.42	0.3	1.7	3.0
11	Pool	8-19 (1800 hrs)	Q003	39.8	29.2	31.0	2.42	2.22	--	0.2	1.2	2.9
11	Sea Surface	8-19 (2100 hrs)	Q008	45.9	22.1	32.0	2.37	2.30	--	0.1	0.8	1.4
11	Sea Surface (thick black)	8-20 (1100 hrs)	Q009	52.7	25.3	22.0	2.53	1.80	--	0.1	1.8	3.2
11	Sea Surface (light brown)	8-20 (1100 hrs)	Q010	46.2	28.6	25.2	2.46	1.85	--	nd	0.9	2.2
11	Sea Surface (light brown)	8-20 (1830 hrs)	Q012	39.9	28.4	31.7	2.29	1.75	--	--	--	--
11	Sea Surface (sheen)	8-22 (1600 hrs)	Q013	50	50	--	2.10	1.37	--	nd	.36	0.40
11	Boom	8-28	Q024	33.2	23.8	43.0	2.23	1.27	--	nd	nd	nd
9	Surface Oil (coalesed)	8-27 (1855 hrs)	Q015	54.5	23.0	22.5	2.11	1.22	--	nd	.1	0.57
9	Diffuser pipe end	8-27 (1600 hrs)	Q019	37.7	24.1	38.8	2.41	2.02	3.47	.2	1.0	2.0
9	Diffuser pipe end	8-27 (1830 hrs)	Q020	43.7	36.8	19.5	2.45	1.91	--	nd	0.7	2.8
9	Surface oil (South of diffuser)	8-27 (2315 hrs)	Q022	47.1	28.4	24.5	2.35	1.31	--	nd	nd	nd
12	Beach	8-28	Q026	38.2	26.0	35.8	2.37	1.32	--	nd	nd	nd

[a]by GC^2/MS

surface sheen sample collected three days after the spill in Bay 11 is more highly weathered (72%) (SHWR = 1.37). Note, however, that the invarient ALK/ISO ratio reflects the lack of biodegradation on the water's surface. An oil sample taken six days later illustrates an SHWR of 1.27 and no change in the ALK/ISO ratio.

Of significance in the Bay 9 oil findings is that of the two samples of oil seen to surface or coalesce (Q015, Q022, Table 3-1) both samples appear highly weathered vis-a-vis loss of light alkanes (SHWR = 1.22 and 1.31, respectively) . These samples are relatively "young" samples, yet have been apparently stripped of light (soluble) saturates in the water column before rising to the surface. Thus the coalesced oil following chemical dispersion has apparently been subjected to accelerated weathering.

The extent of weathering is also noted by the absolute concentration of the highly weatherable naphthalene series. Where the SHWR equals 1.4 or less, the naphthalenes are much reduced in concentration. Below a SHWR of 1.3 naphthalenes are not detected. Note that the coalesced oils are stripped of their light aromatics (i.e., naphthalenes) as well.

3.1.2 Oil in the Water Column

3.1.2.1 Low Molecular Weight Hydrocarbons

The content and composition of low molecular weight hydrocarbons (LMWHC) in seawater samples from the test bays was determined on 73 samples.

3.1.2.la Bay 9

Many of the LMWHC samples were obtained from Bay 9 during the discharge of the dispersed oil (August 27, 1400-2000 hours) and through 2400 hours on August 27. Instantaneous LMWHC concentrations ranged from background levels (~30-50 ppb) to 9,100 ppb. The conversion of LMWHC concentrations to "total oil concentrations" is roughly a factor of three to four. Concentrations in the bottom waters along the two shoreline transects, SS1 and SS2 (see Figure 3.1) are presented in Table 3-2. The data are more easily visualized when viewed in a series of Bay 9 schematics (Figures 3.2 through 3.11). Not all stations were sampled at all times between 1300 and 2400 hours on August 27, but several trends emerge. Highest concentrations appeared in bottom waters at the 10m (SS1) station. Marked vertical concentration differences were seen at the Baffin Queen Station beginning at 1400 hours. Initially (1400 hours) background levels of oil were seen at the 3 m station (ss1). With time these concentrations increased to a high of 840 ppb when sampled at 2300 hours. Elevated LMWHC values (300-400 ppb) were still observed in samples taken on August 28 (1100 and 1600 hours), but soon thereafter the LMWHC levels decreased to background levels (30-50 ppb). No detectable LMWHC were observed on either August 29 (3 samples) or August 30 (4 samples), two and three days after the spill.

Gas chromatographic traces of LMWHC compounds in the samples (e.g., Figure 3.12) can be converted to compositional plots (Figures 3.13 through 3.16) to reveal the major components in the samples. At lower levels (300-400 ppb) the predominant components found were the C6 through C9 straight and branched alkanes, and the alkylated benzenes, toluene, ethyl benzene and xylene. At higher concentrations the C7 through C9 alkanes became the most dominant grouping with

Table 3-2. Low molecular weight hydrocarbon results (in ppb)

Bay	Station	Date	Depth (m)	Time	n-hexane	C7, C8, C9 Alkanes	Decane	Benzene	Toluene	Ethyl benzene
Bay 9	55-1	Aug. 27	3	1500	37	284	10	2	16	15
		Aug. 27	3	1900	31	218	2	tr	16	15
		Aug. 27	3	2300	43	529	56	6	22	29
		Aug. 30	3	1600						
		Aug. 30	3	1700						
	55-1	Aug. 27	7	1400			5	tr	tr	3
		Aug. 29	7	1200	8	25		tr	3	
		Aug. 29	7	1700	3	20		tr		
	SS-1	Aug. 27	10	1900	65	89	10	3	12	12
		Aug. 27	10	2100	290	1470	125	35	185	94
		Aug. 30	10	1700						
	55-2	Aug. 27	3	1400		9		tr	tr	9
		Aug. 27	3	2300	78	360	12	6	33	27
		Aug. 29	3	1200		23		tr	12	
	SS-2	Aug. 27	7	1300	40	1400	210	44	27	51
	55-2	Aug. 27	10	1300	50	1300	200	34	35	8
		Aug. 27	10	1600	740	4600	390	135	625	195
		Aug. 27	10	1700	510	2250	24	58	370	105
		Aug. 27	10	2100		240	22			17
		Aug. 27	10	2300	120	630	22	tr	56	120
		Aug. 28	10	1600	5	10	10		16	24
		Aug. 29	10	1200	5	30		tr	4	13
	BQ	Aug. 27	0	1400		10		tr		10
		Aug. 27	0	1600	36	210	10	4	14	15
		Aug. 27	0	1800	39	250	10	3	18	32
		Aug. 27	0	2100	39	220	7	tr	15	10
		Aug. 27	0	2400	71	400	35	11	36	15
	BQ	Aug. 27	2	1400		20		3	3	
		Aug. 27	2	1600	30	203	9	tr	13	11
		Aug. 27	2	1800	59	368	14	5	25	42
		Aug. 27	2	2400		59	4	3	tr	5
	BQ	Aug. 27	4	1400	12	128			9	6
		Aug. 27	4	2100	tr	60		tr	tr	14
		Aug. 27	4	2300	tr	32		tr	tr	5
		Aug. 27	4	2400	390	2900	310	51	240	89
	BQ	Aug. 27	6	1400	28	195	10	tr	14	14
		Aug. 27	6	1600	175	1000	76	17	95	63
		Aug. 27	6	1800	200	940	38	18	120	67
		Aug. 27	6	2100	140	570	38	17	52	49
		Aug. 27	6	2300	13	130		5	8	11
		Aug. 27	6	2400	59	200	16	10	44	33
	n-micro	Aug. 27	9-1o	0200					3	−
		Aug. 28	11-12	1100						
	s-micro	Aug. 27	9-1o	0100						

(−) = none detected (<1 ppb)
tr = trace (<1 ppb)

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Bay	Station	Date	Depth	Time	p, m xylenes	Cumene	O-xylene	1,2,4 trimethyl benzene	Other alkyl benzenes	Unknown volatiles	TOTAL
Bay 9	SS-1	Aug. 27	3	1500	16		9	8	12		409
		Aug. 27	3	1900	2				21		305
		Aug. 27	3	2300	11		22	8	116		842
		Aug. 30	3	1600						38	38
		Aug. 30	3	1700						17	17
	Ss-1	Aug. 27	7	1400						48	58
		Aug. 29	7	1200						5	42
		Aug. 29	7	1700							25
	SS-1	Aug. 27	10	1900	11		4		16	−	222
		Aug. 27	10	2100	190	30	86	88	315	320	3228
		Aug. 30	10	1700	17	−				9	26
	SS-2	Aug. 27	3	1400	tr					5	23
		Aug. 27	3	2300	41	7	18	18	26	10	636
		Aug. 29	3	1200				3		−	38
	SS-2	Aug. 27	7	1300	30		15	18	100	480	2415
	SS-2	Aug. 27	10	1300	20		11	10	50	420	2138
		Aug. 27	10	1600	570	94	260	210	570	530	8919
		Aug. 27	10	1700	440	25	146	105	260	230	4523
		Aug. 27	10	2100	5		8	5	50	20	367
		Aug. 27	10	2300	20	10	69	27	100	20	1194
		Aug. 28	10	1600	20		15	10	40	10	120
		Aug. 29	10	1200							52
	BQ	Aug. 27	0	1400	3					10	33
		Aug. 27	0	1600	16		11	3	30		349
		Aug. 27	0	1800	32	25	28	15	27	10	489
		Aug. 27	0	2100	15		10	6	15		337
		Aug. 27	0	2400	40	20	22	14	40	33	737
	BQ	Aug. 27	2	1400	3			4	−	21	54
		Aug. 27	2	1600	12		8	3	22		311
		Aug. 27	2	1800	48	41	54	13	80	10	759
		Auq. 27	2	2400	−	−			18		89
	BQ	Aug. 27	4	1400	14		tr		17	−	186
		Aug. 27	4	2100	tr		tr	tr	17		91
		Aug. 27	4	2300	tr			6	18		61
		Aug. 27	4	2400	290	60	135	145	370	375	5325
Bay 9	BQ	Aug. 27	6	1400	13		7	6	17	10	314
		Aug. 27	6	1600	120	19	56	56	95	81	1853
		Aug. 27	6	1800	150	38	78	40	165	40	1894
		Aug. 27	6	2100	81	40	57	36	69	70	1221
		Aug. 27	6	2300	11		11	5	18	10	222
		Aug. 27	6	2400	62	5	23	30	38	10	530
	n-micro	Aug. 27	9-1o	0200				12		4	19
		Aug. 28	11-12	1100						50	50
	s-micro	Aug. 27	9-1o	0100						38	38

Table 3-2 (Continued). Low molecular weight hydrocarbon results

Bay	Station	Date	Depth	Time	p, m xylenes	Cumene	O-xylene	1,2,4 trimethyl benzene	Other alkyl benzenes	Unknown volatiles	TOTAL
Bay 11	Ss-1	Aug. 20	3 m	900	10				3	5	53
		Aug. 20	3m	1000	3				4	5	57
		Aug. 20	3 m	1100						39	39
		Aug. 20	3 m	1200					3	26	43
		Aug. 20	3 m	1600			-	4		20	46
	SS-2	Aug. 20	3 m	1000				-		32	59
		Aug. 20	7 m	1000							13
	n-boom	Aug. 20	2-4 m	1500		-			1	3	14
	s-boom	Aug. 20									
	mid-boom	Aug. 20	0-2 m	1600	-			-	3	2	23
	n-micro	Aug. 20	0-2 m	1700	6		3	28	3		72
	n-micro	Aug. 20	11.0 m	1700						8	8
Bay 10	n-micro	Aug. 28	3-4 m	2000	3		3	-	14		164
			5-6 m	0200	90	tr	43	10	190	112	1491
			9-10 m	0200	3	-		10			37
	s-micro	Aug. 28	7-8	0100	7		4			9	196
			9-1o	1900	4			-		10	122
			15	1900				14	13		101
		Aug. 29	7-8	0100	10	-	6		19		212
			7-8	1400	28	-	20	tr	48	10	372
	BQ	Aug. 28	2	1800	5			-	10	10	146
			2	1800	tr				13	-	155
			4	1800	4	-	tr	-	6		71
		Aug. 29	6	1300	10		5	7	8	-	213

-65-

Table 3-2 (Continued).   Low molecular weight hydrocarbon results

Bay	Station	Date	Depth	Time	n-hexane	C_7, C_8, C_9 Alkanes	Decane	Benzene	Toluene	Ethyl benzene
Bay 11	Ss-1	Aug. 20	3 m	900		25	3	3	5	3
		Aug. 20	3 m	1000		27		2	3	13
		Aug. 20	3m	1100						
		Aug. 20	3 m	1200				2		12
		Aug. 20	3 m	1600		8	6	2		6
	SS-2	Aug. 20	3 m	1000	–	20		2		5
		Aug. 20	7 m	1000			4	2		7
	n-boom	Aug. 20	2-4 m	1500	–	10			–	
	s-boom	Aug. 20								
	mid-boom	Aug. 20	0-2 m	1600		11	1		2	4
	n-micro	Aug. 20	0-2 m	1700		16	8	3	5	
	n-micro	Aug. 20	11.0 m	1700						
Bay 10	n-micro	Aug. 28	3-4 m	2000	6	120	5	4	4	5
			5-6 m	0200	45	780	110	12	72	27
			9-10 m	0200	tr	17			tr	7
	s-micro	Aug. 28	7-8	0100		150	6		10	10
			9-1o	1900	5	90	5	3	5	tr
			15	1900		63	6	tr	tr	5
		Aug. 29	7-8	0100	12	140	9	tr	11	5
			7-8	1400	13	200	10	tr	18	25
	BQ	Aug. 28	2	1800	7	92	6	4	5	7
			2	1800	8	117	10	3	4	
			4	1800	4	42	tr		5	10
		Aug. 29	6	1300	5	147	7	tr	12	12
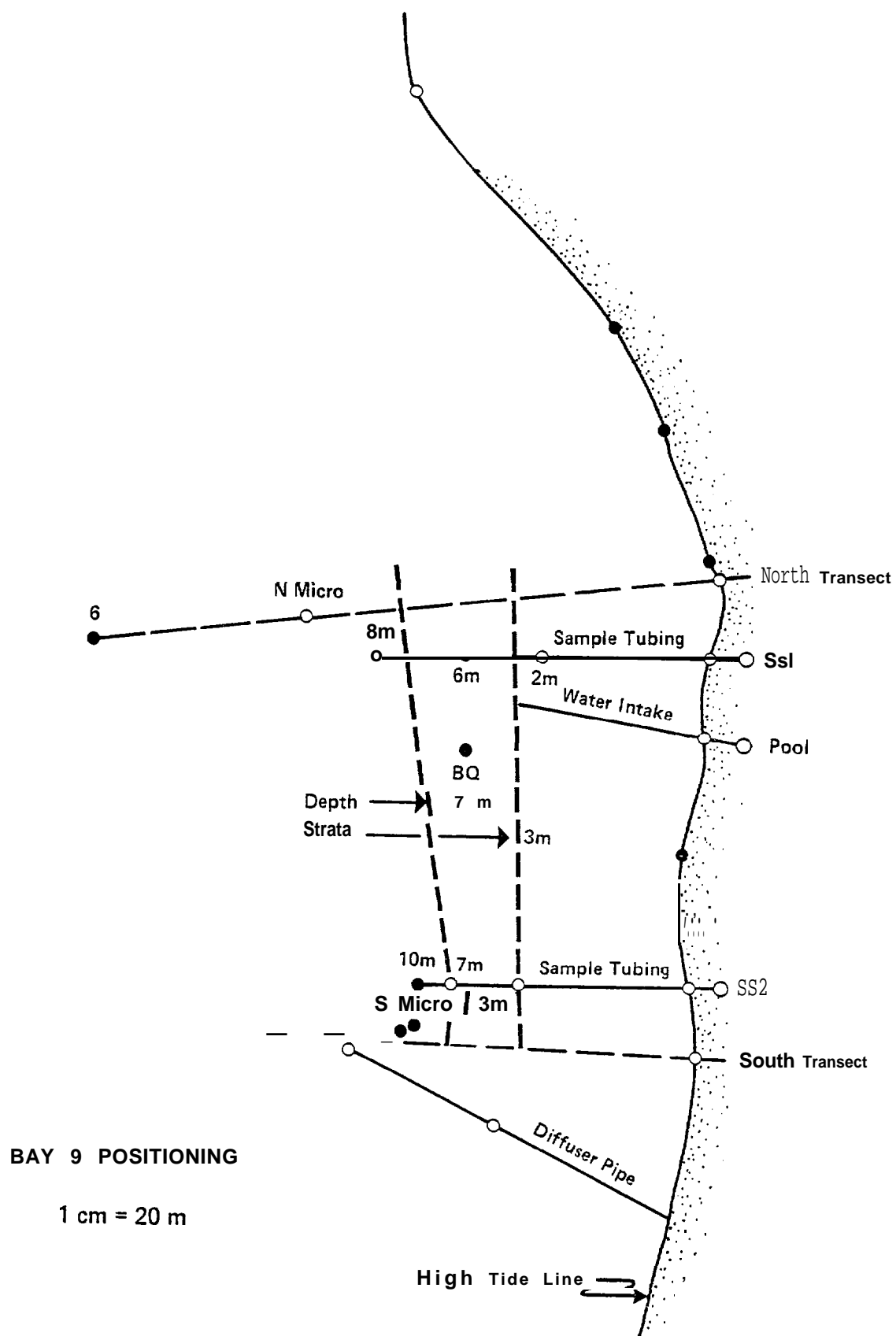
Figure 3.1. Location of Sampling Points within Experimental Bays (Bay 9).
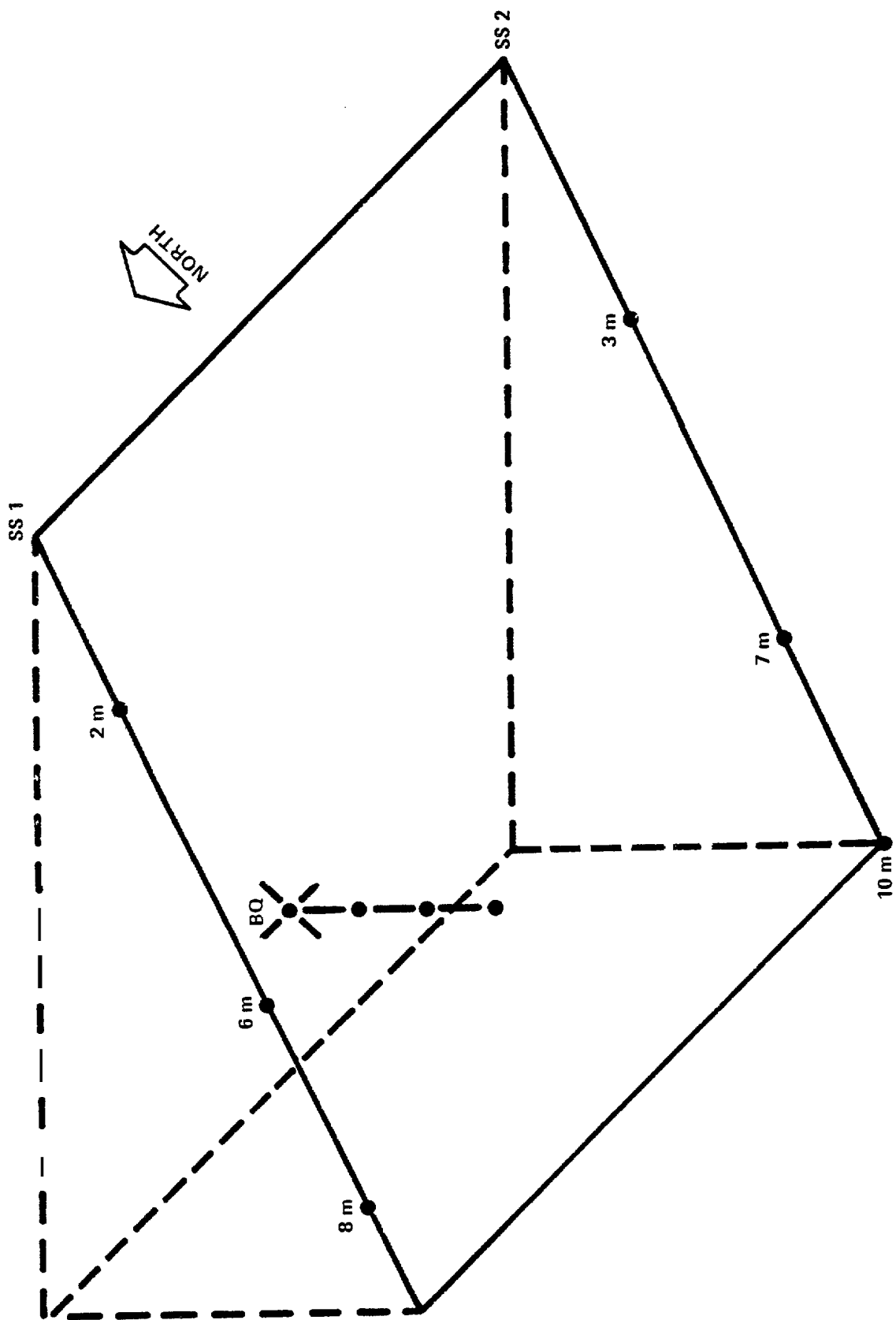
Figure 3.2. Bottom Water Sampling Pumps from Shore Points and Barge Queen Profiling.

NORTH

27 AUG 8'
1,300
T=0

2,415

2,140
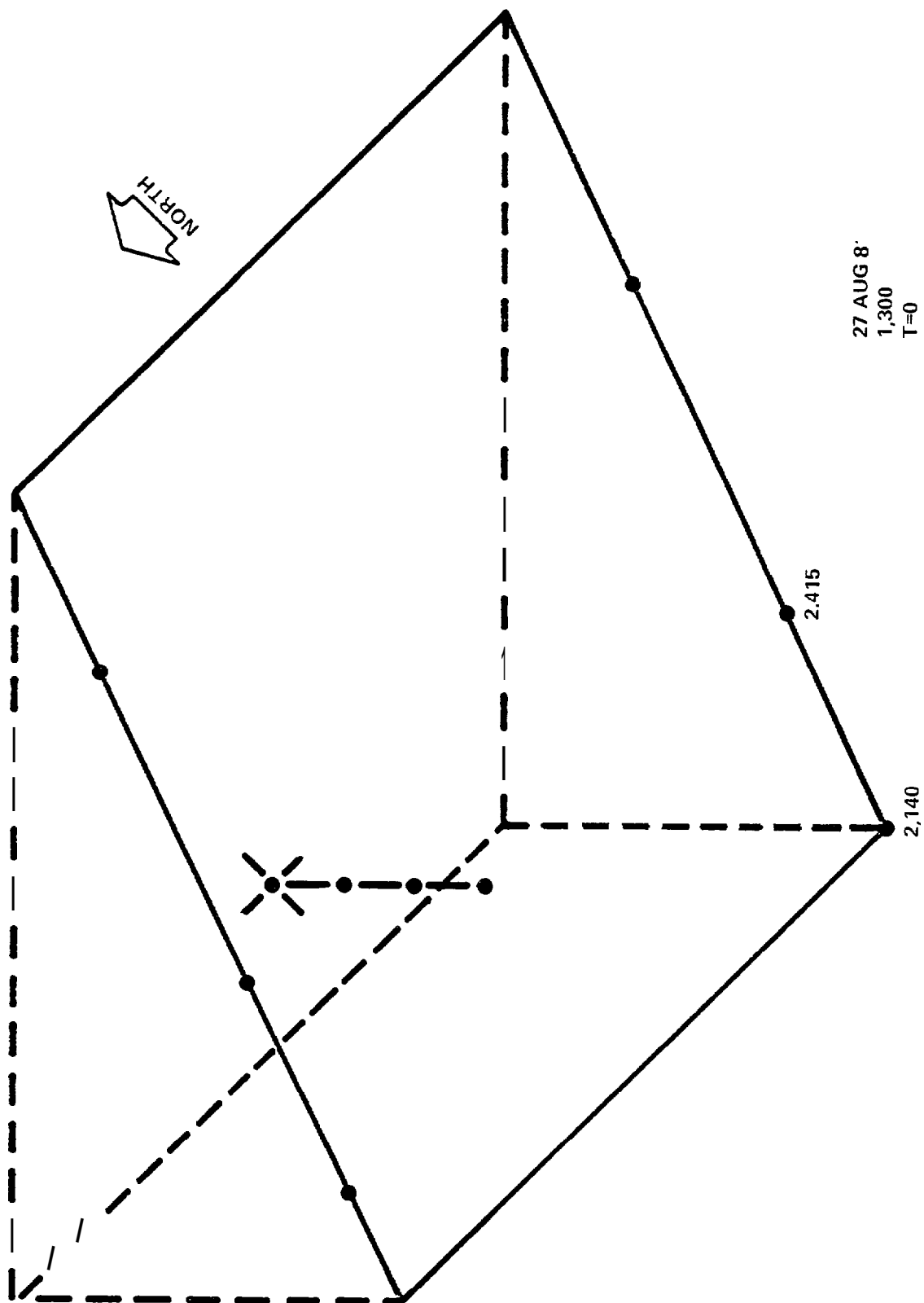
Figure 3.3. Bay 9 LMW Hydrocarbons (Hours).
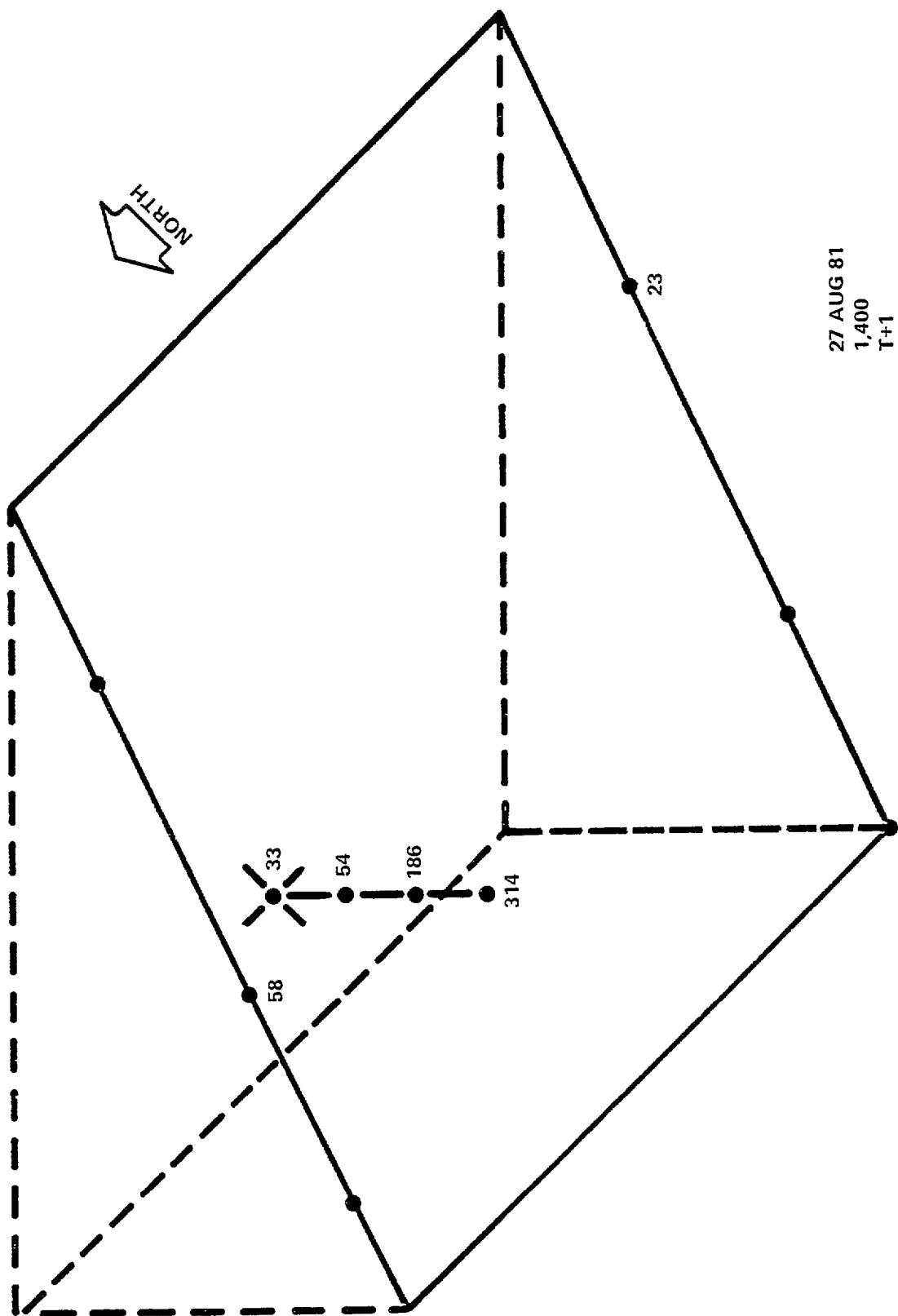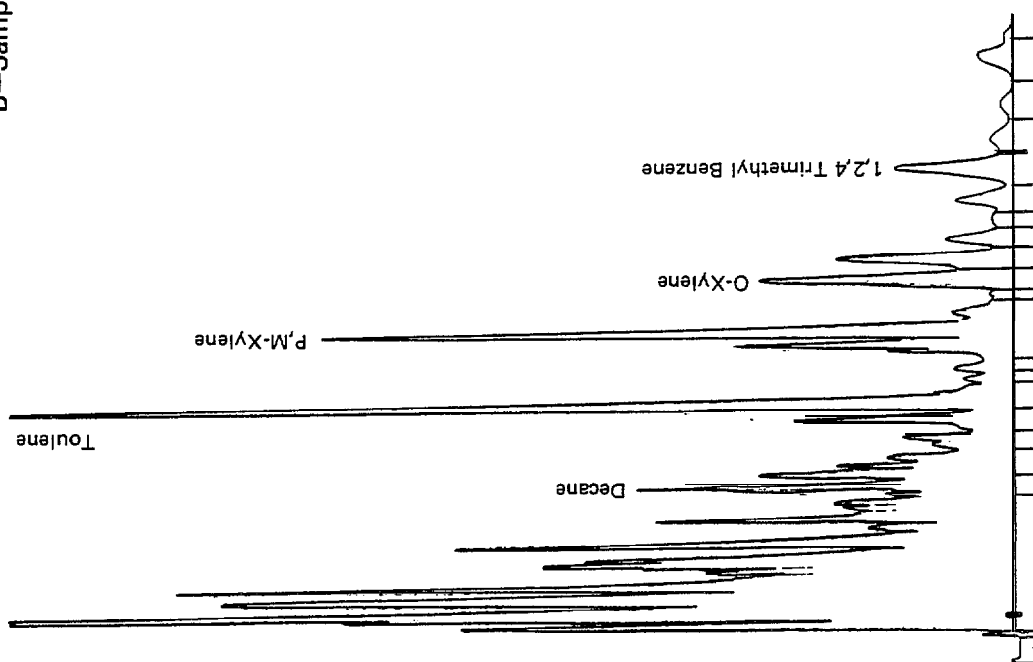
Figure 3.4. Bay 9 LMW Hydrocarbons (1400 Hours).
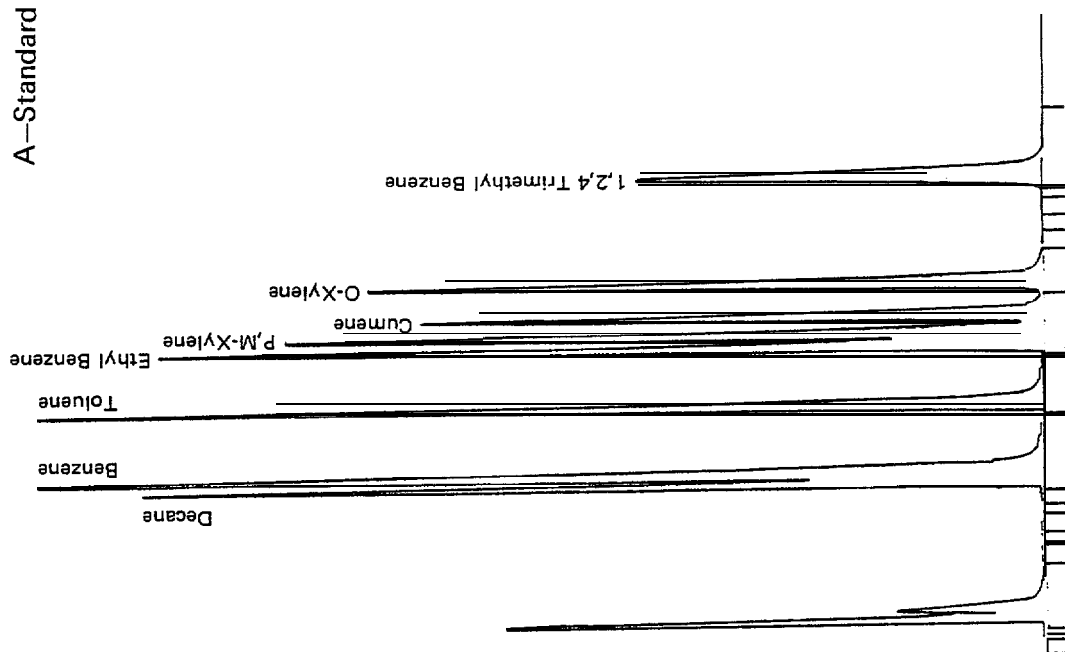
27 AUG 81
1,400
T+1

NORTH

33
54
186
314
58
23

NORTH

27 AUG 81
1,600
T+3

350

300

1,850

8,900
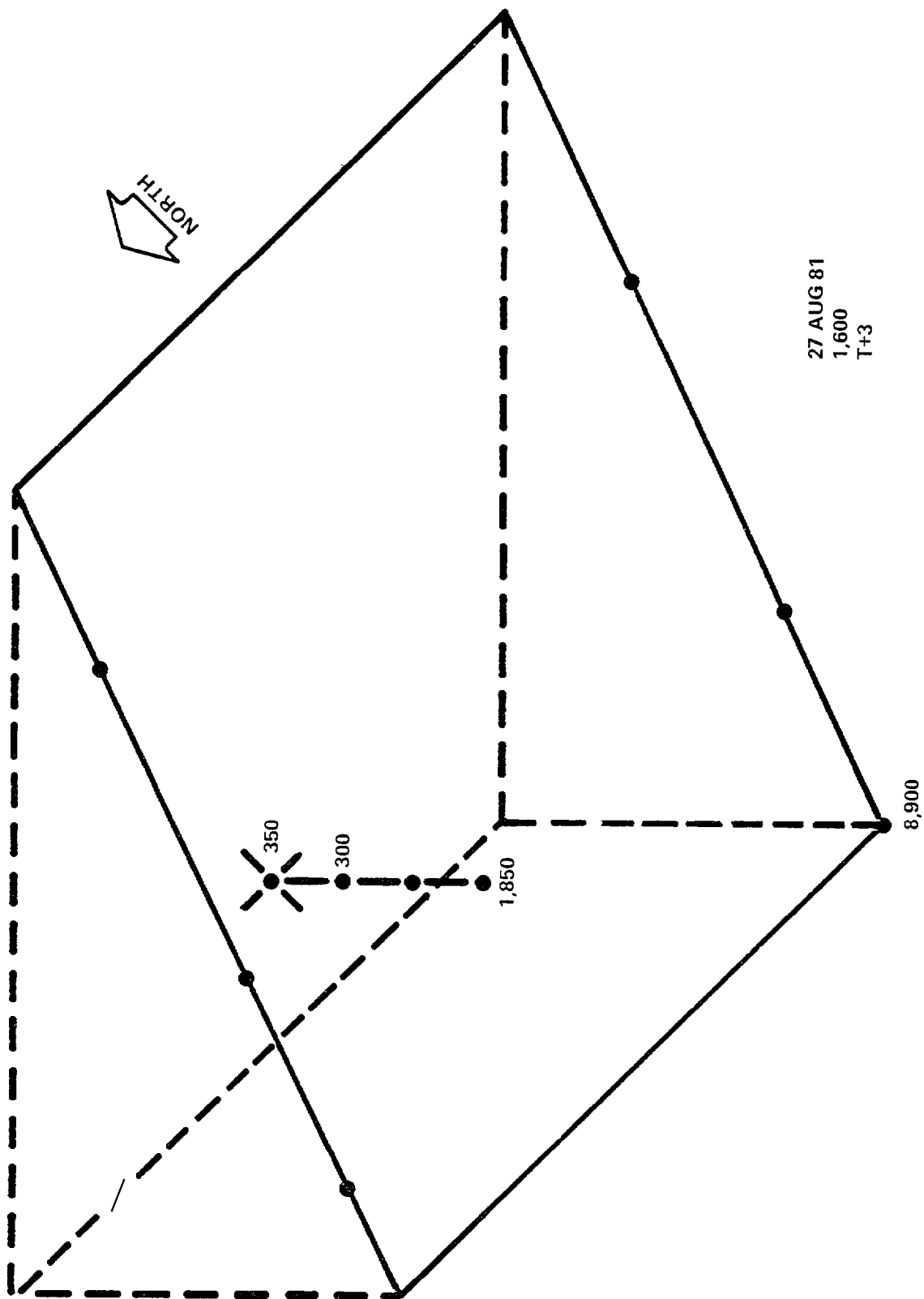
Figure 3.5. Bay 9 LMW Hydrocarbons (1600 Hours).

NORTH

27 AUG 81
1,800
T+5

49○
760
—
1,890
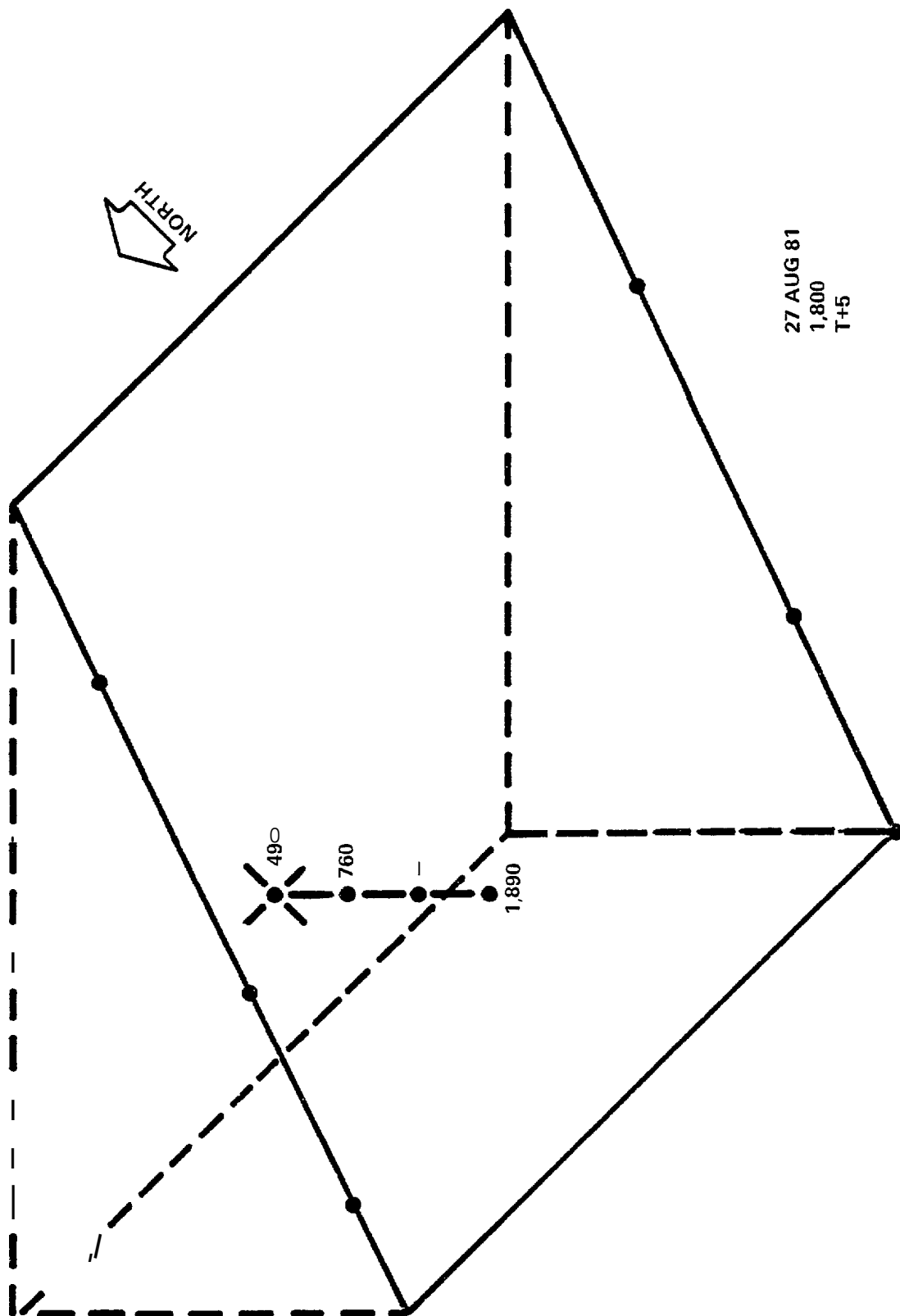
Figure 3.6. Bay 9 LMW Hydrocarbons (1800 Hours).

NORTH

27 AUG 81
1,900
T+6

305

220
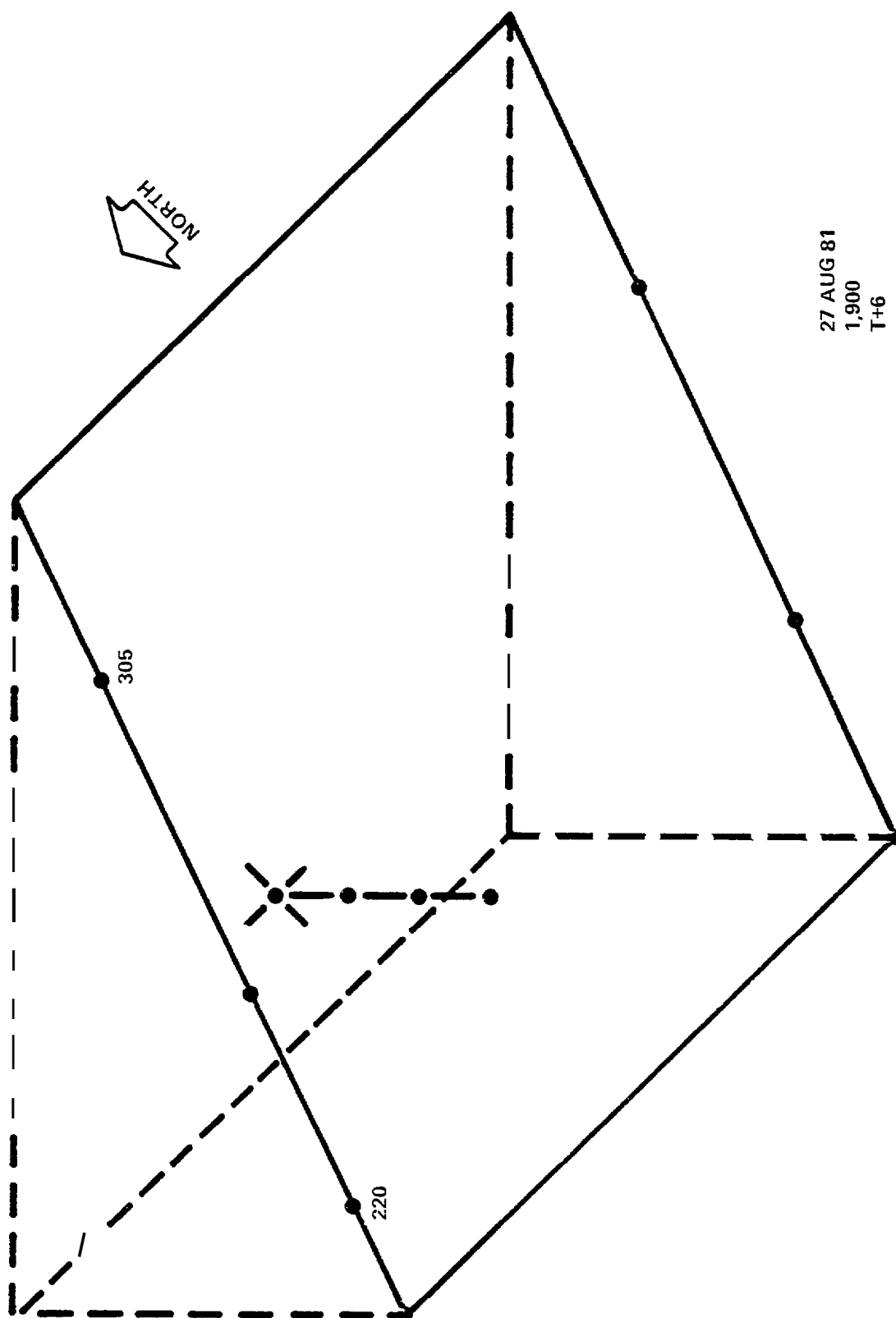
Figure 3.7. Bay 9 LMW Hydrocarbons (1900 Hours)
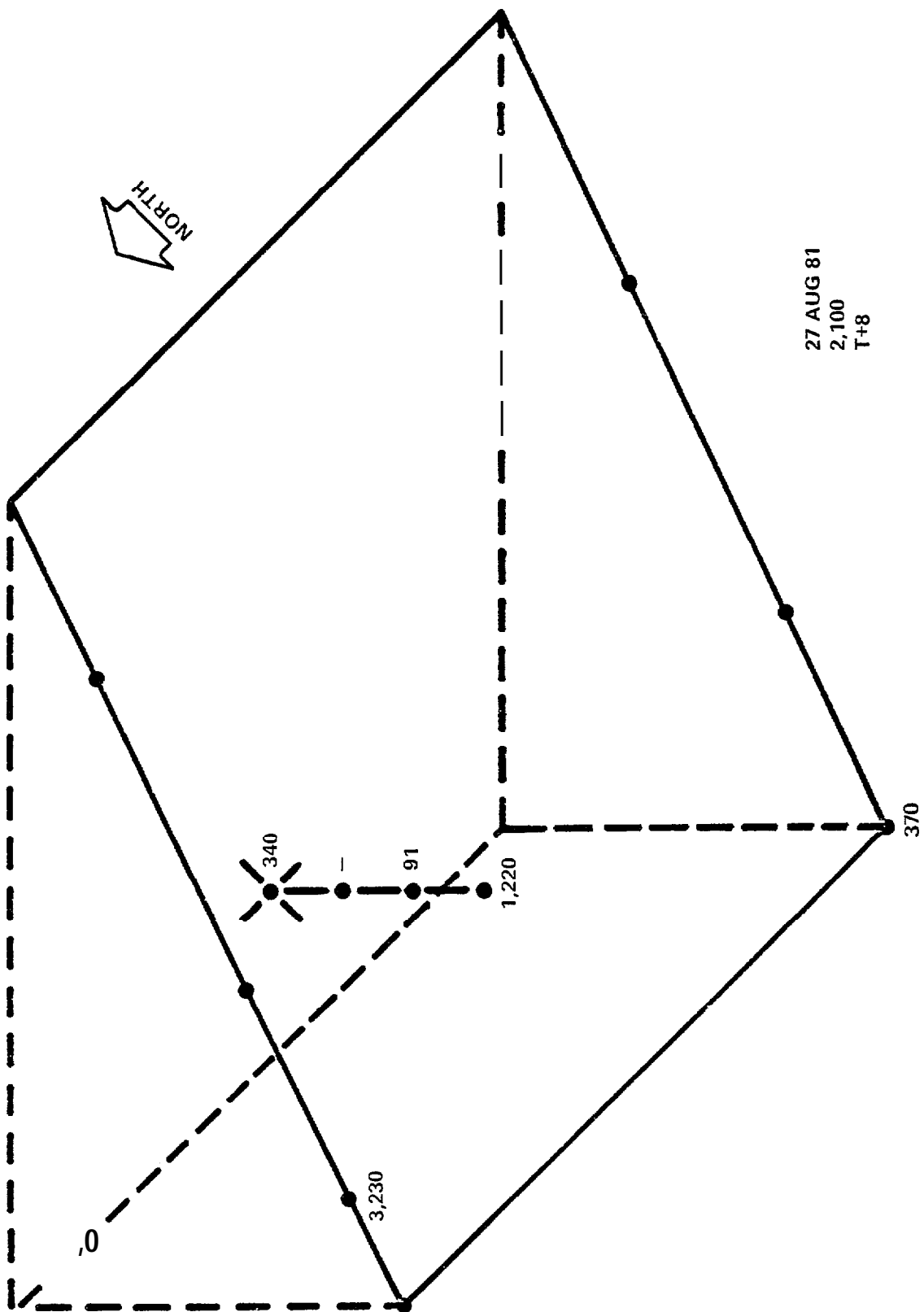
Figure 3.8. Bay 9 LMW Hydrocarbons (2100 Hours).

NORTH

27 AUG 81
2,100
T+8

340

91

1,220

370

3,230

,0
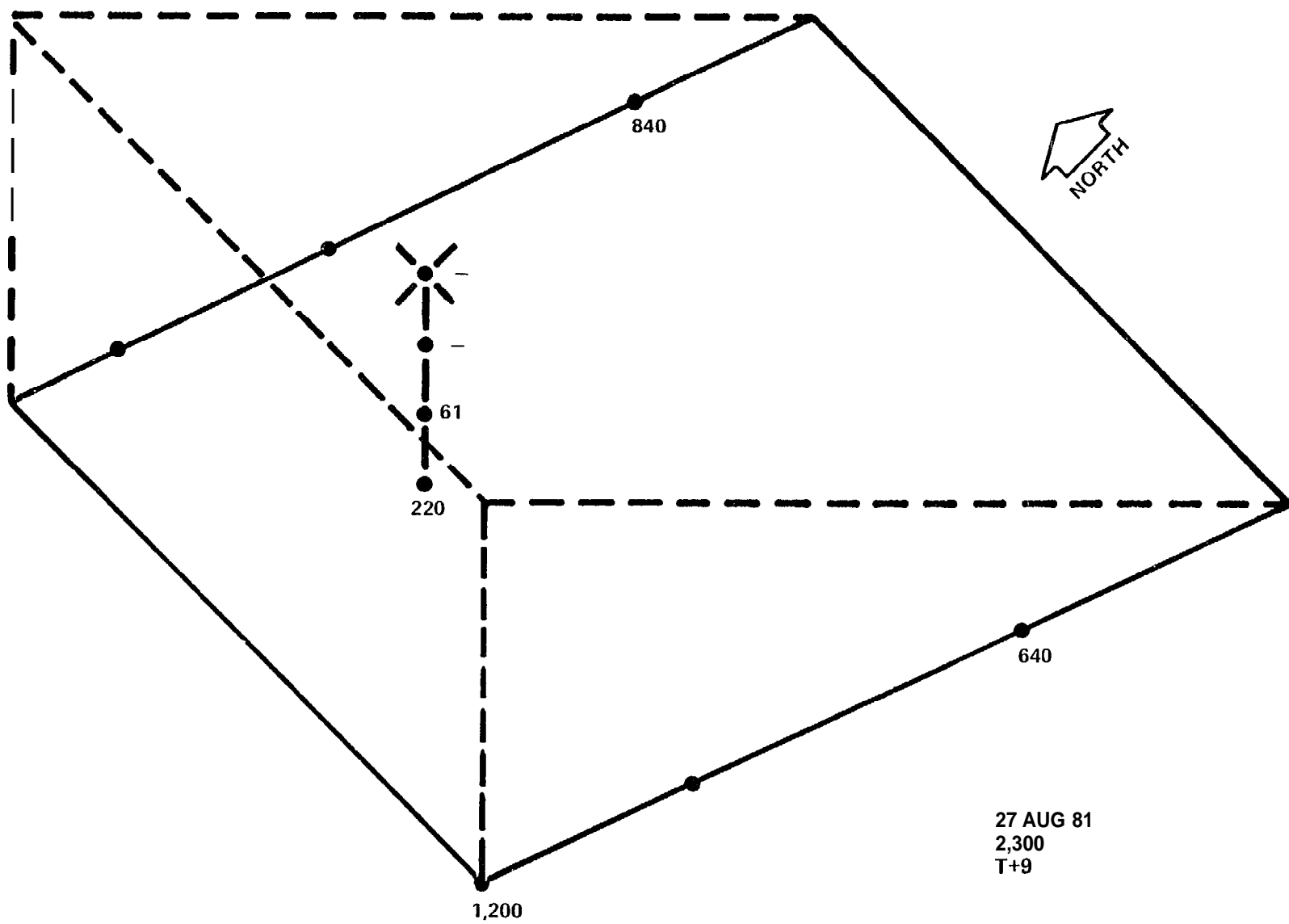
Figure 3.9. Bay 9 LMW Hydrocarbons (2300 Hours).

NORTH

27 AUG 81
2,400
T+11

740

90

5,300

530
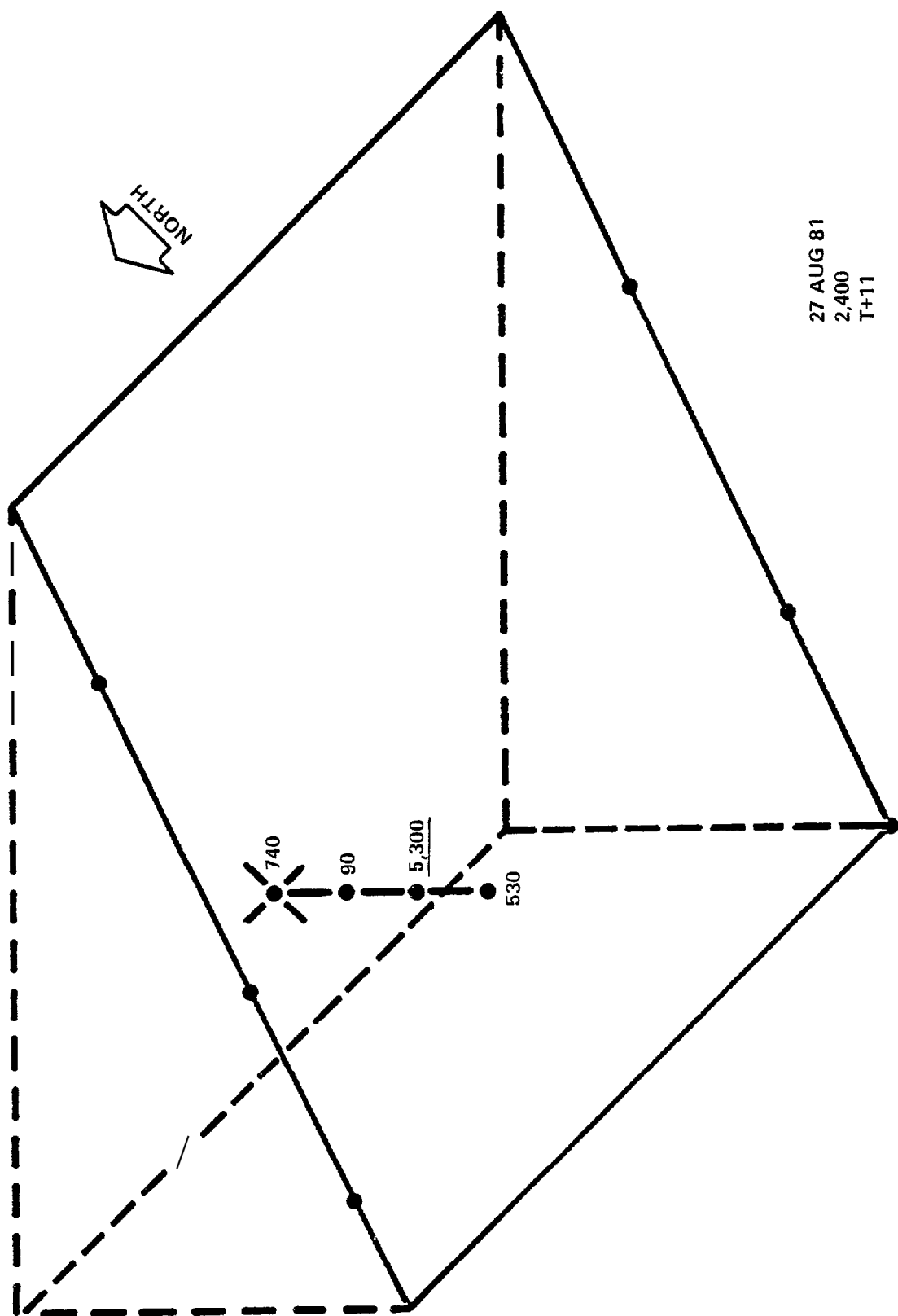
Figure 3. 0. Bay 9 LMW Hydrocarbons (2400 Hours).
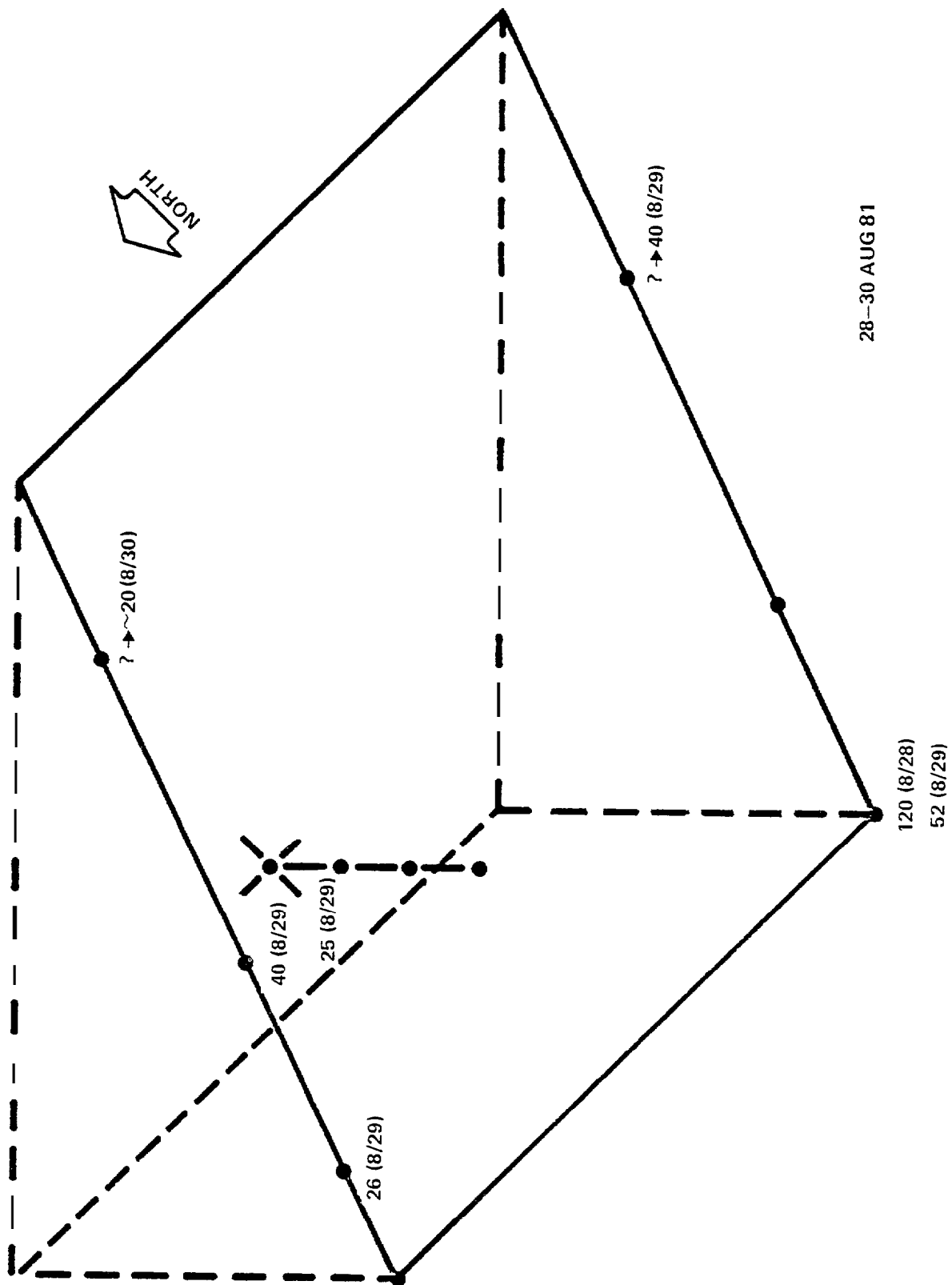
Figure 3.1 Bay 9 Hydrocarbons (28—30 August)

NORTH

? → 40 (8/29)

28—30 AUG 81

? → ~20 (8/30)

120 (8/28)

52 (8/29)

40 (8/29)

25 (8/29)

26 (8/29)

B—Sample

1,2,4 Trimethyl Benzene

O-Xylene

P,M-Xylene

Toluene

Decane

A—Standard

1,2,4 Trimethyl Benzene

O-Xylene

Cumene

P,M-Xylene

Ethyl Benzene

Toluene

Benzene

Decane

MW   G

-78-
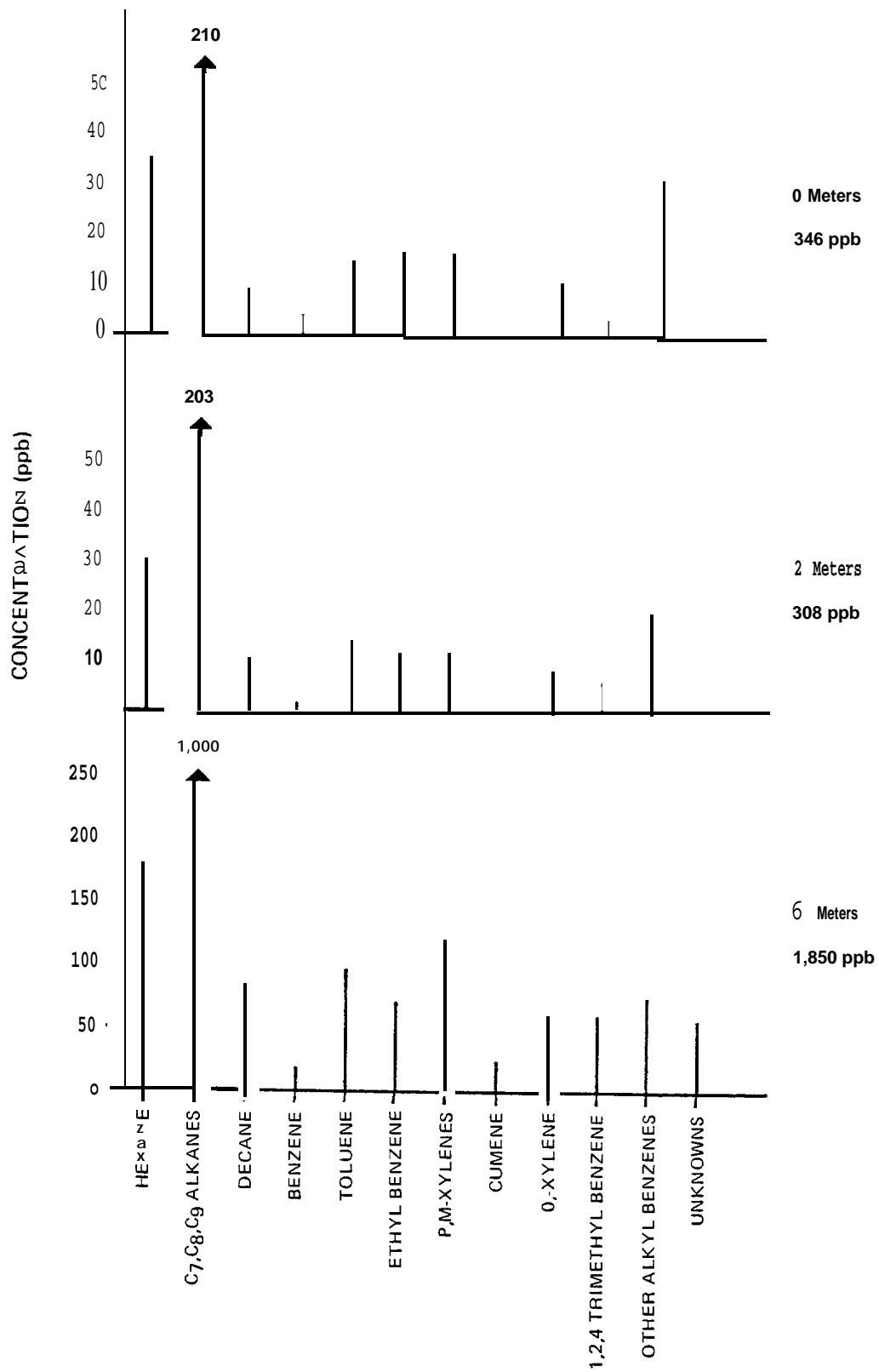
Figure 3.13. Baffin Queen; 1600 Hours, 27 August 1981.
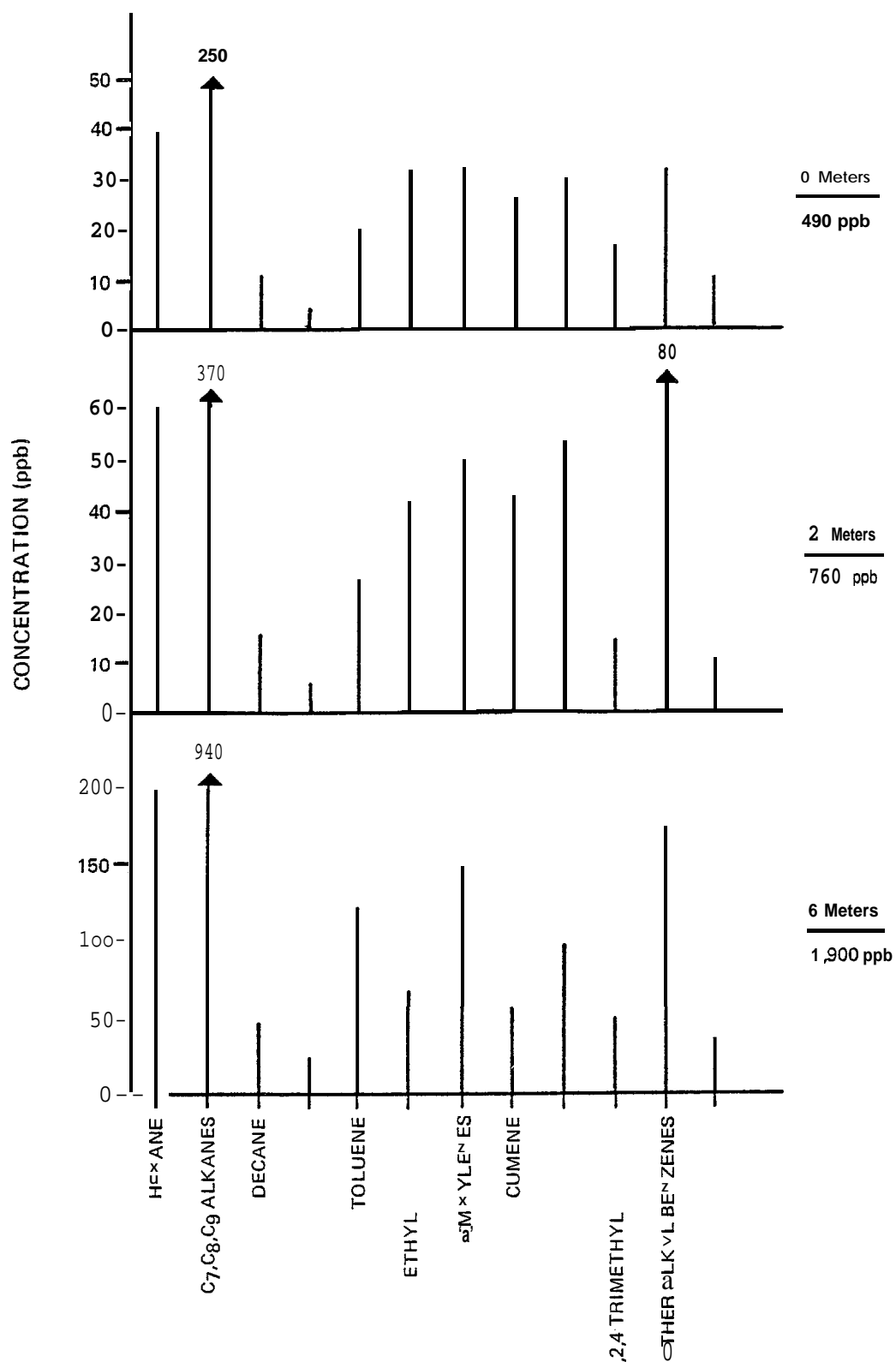
Figure 3.14. Baffin Queen: 1800 **Hours, 27 August 1981.**
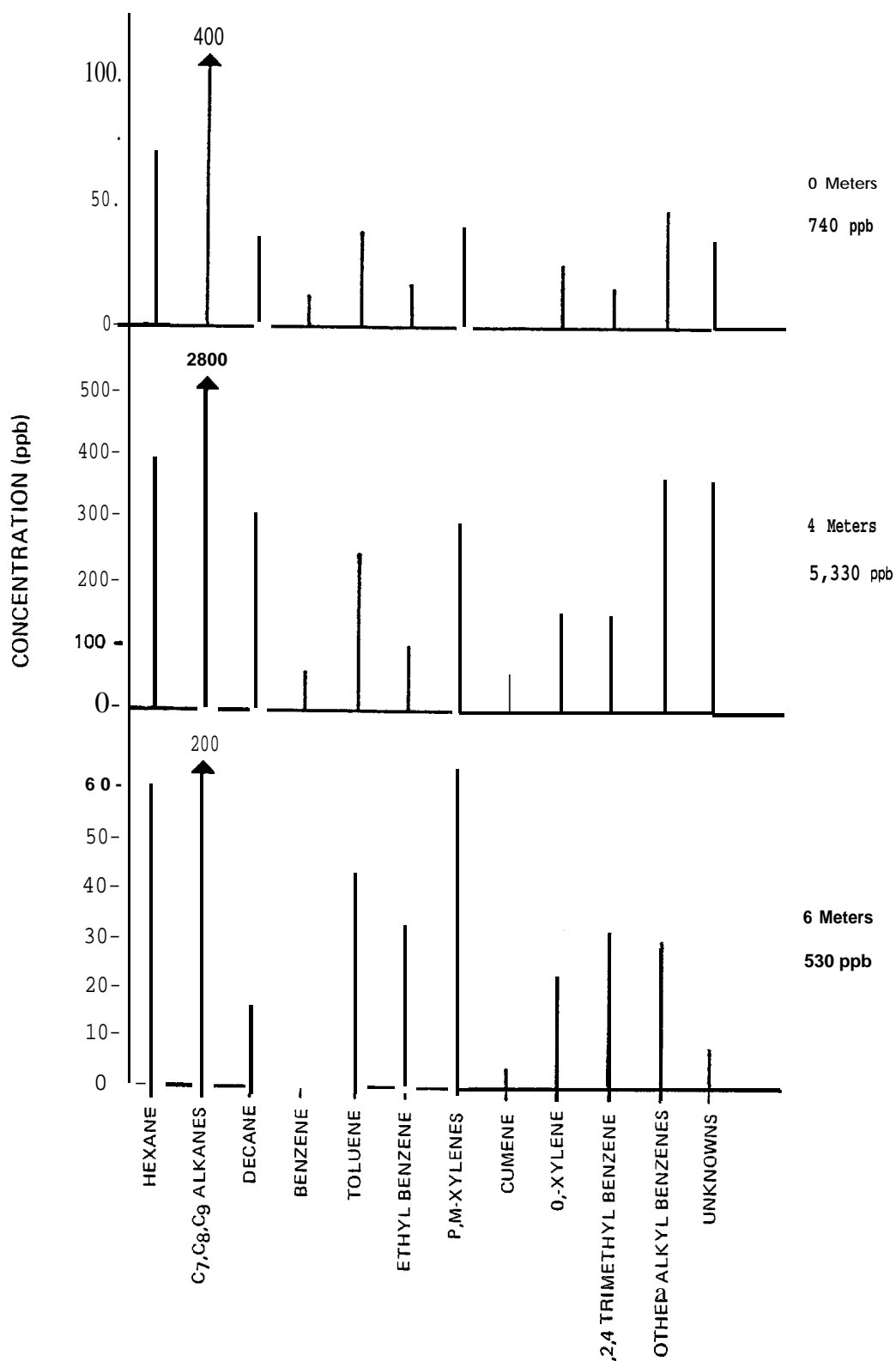
Figure 3.15. Baffin Queen; 2400 **Hours, 27 August 1981.**
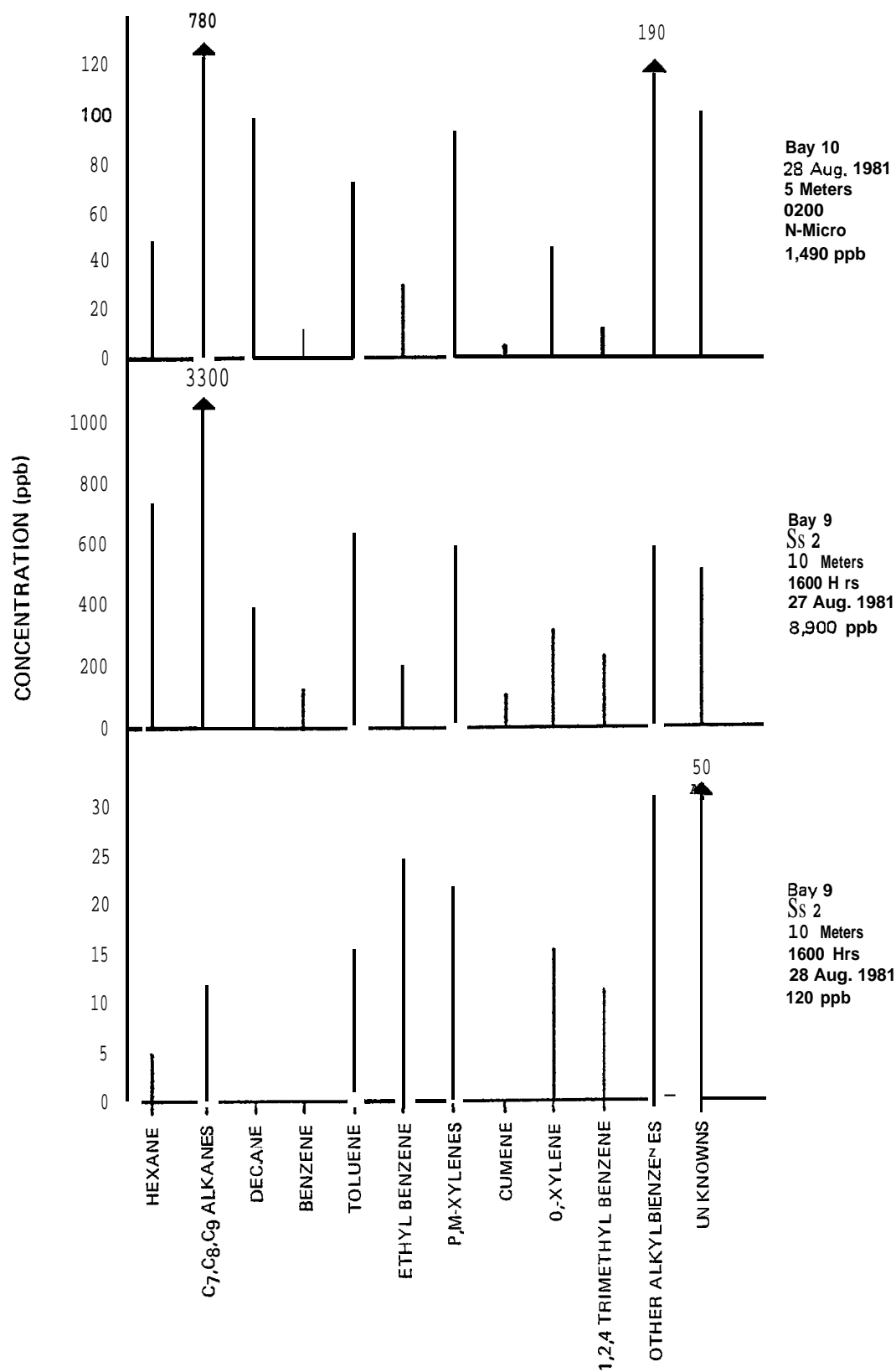
Figure 3.16. LMWHC: Various Stations & Times.

a variety of alkylated benzenes and low levels of benzene
itself present. Note the compositional variations within
the water column that were seen where large concentration
differences exist (Figure 3-13). However, where concentra-
tions are above 500 ppb, a full suite of LMWHC (Figure 3-15)
was detected and the composition changes little with in-
creasing concentration. Note in Figure 3-15 the order of
magnitude increase observed in LMWHC concentration at
mid-depth with virtually no change in composition. That
this uniformity of composition persists, a composition which
is very similar to the dispersed oil when it first emerges
from the diffuser system, and characterizes samples that
have been waterborne for at least five hours (see Figure 3-15;
2400 hours) indicates that dispersed oil droplets (i.e.,
whole unfractionated oil) persist in the system for many
hours with little evaporative loss of the LMWHC during
the dispersed oil's residence in the water column.

3.1.2.1b Bay 10

A series of 12 LMWHC samples was taken at three loca-
tions and at various times at Bay 10 (Table 3-2). Several
results are noteworthy. A distinct midwater plume of oil
moving northward out of Bay 9 and through Bay 10 is detected
at the N-micro station at 5-6 m depth. The observed oil
concentration was 1500 ppb, but the concentration at the
9-10 m depth was only near background at the same time.
Concentrations were somewhat elevated at the S-micro station
at 0100 hours (August 28) at 7-8 m depth (200 ppb). That
LMWHC persisted in the Bay 10 system through August 28 is
evident from the modest elevations in LMWHC levels
(100-300 ppb) in all samples taken during August 28. In
samples taken at 1300 and 1400 hours on the 28th, levels of

LMWHC were ∿300 ppb with a low-level composition very
similar to that observed in Bay 9 (see Table 3-2). No
samples were taken after 1400 hours on August 28 in Bay 10.

3.1.2.1c Bay 11

Eleven samples were taken between 1800 hours on
August 19 and 1700 hours on August 20 for bottom water oil
concentration determinations in Bay 11. Only very low
levels (background to ∿100 ppb) were observed in these
samples. LMWHC were elevated in surface waters (e.g.,
mid-boom station O-3 m; 1600 hours; 20 August) when sampled
(∿150 ppb), but in general water column levels of LMWHC in
Bay 11 were quite low (<10 ppb).

Bay 11 was also sampled for LMWHC at 1100 and 1500 hours
on August 29. Levels of LMWHC in the water column were in the
80-350 ppb range indicating either continued "leaching" of oil
off of the Bay 11 beach or persistent low-level cross contam-
ination from the dispersed oil spill. LMWHC levels at **Bay 10**
during the same time period were also ∿350 ppb. Therefore, we
have no way of discerning which of the above explanations is
most plausible.

3.1.2.2 High Molecular Weight Hydrocarbons (4 Liter Samples)

A wide variety of unfiltered water samples was obtained
for analysis to determine (by GC^2) hydrocarbon concentra-
tions in the water column and to examine compositional
changes in the oil. Additionally, analytical work has been
performed on the chemical composition of Corexit 9527 disper-
sant.

3.1.2.2a <u>Bay 9</u>

Not surprisingly, oil concentrations in Bay 9 were observed to be the highest of any in the study (Table 3-3). Although the discharge of dispersed oil began at 1400 hours, concentrations were generally low at Baffin Queen (BQ) and SS1 (3 and 7 meters) stations (see Figure 3-1) during the first hours of the spill. Oil at concentrations of ~12 ppm were, however, observed at 1400 hours at the SS2 (10 m) station closest to the discharge pipe. Concentrations at BQ were highest between 1800 and 2400 hours when midwater and bottom water values were 2 to 6 ppm. Similarly, the 1800 and 2300/2400 hours samples at SS1 and SS2 contained high (5-44 ppm) concentrations of oil. Concentration levels remained in the 200 to 400 ppb range through August 29 and thereafter decreased to background levels, as evidence by samples taken at the microbiology stations (H5, H6).

That **compositionally** unaltered oil remained in the system for at least several days (i.e., through August 29) is indicated by the GC^2 data which for the most part reveal only a lightly weathered saturated hydrocarbon assemblage, with **SHWR** values of 2.1 to 2.6. Figure 3-17 illustrates the composition of the oil (**SHWR=2.2**) present in the water column (H5; N-micro) on **August** 29. Some moderate weathering did occur where oil levels were low or moderate, such as with the anomalous 2-meter Baffin Queen sample (**SHWR=1.0**; 2300 hours) "sandwiched" by fresher oil (**SHWR=2.2,2.3**) above and below (Figure 3-18). Additionally there is evidence for subsurface plumes with enhanced concentrations of the water soluble aromatics as evidenced in Table 3-3 by the AWR value of 5.3 occurring at 4 meters in the Baffin Queen series.

TABLE 3-3

BAY 9 HMWHC DATA - WATER

STATION	DATE	DEPTH	TIME	CONC. (μg/L)	SHWR	AWR[a]
BQ	8/27	0	1400	1.1	1.4	
		2	1400	125.0	2.2	
		4	1400	100.0	2.2	
		6	1400	~500	1.4	
		0	1800	1400	2.3	2.2
		2	1800	1400	2.1	
		4	1800	4800	2.4	3.1
		6	1800	5800	2.4	3.0
		0	2400	1750	2.2	3.3
		2	2300	68.0	1.0	
		4	2400	4500	2.3	5.3
		6	2400	2700	2.1	
Ss 1	8/27	3(bottom)	1600	25.0	---	
		7 (")	1400	8.0	1.3	
		10 (")	2300	4900	2.1	
Ss 2	8/27	7(bottom)	1400	8400	2.2	
		10	1400	11800	2.4	4.7
		3	1800	3100	2.6	
		10	1800	40000	2.4	4.1
		10	2300	2800	2.6	2.4
	8/28	10	1600	180	1.9	
N-Micro (H5)	8/29	5	---	350	2.2	
	9/3	5		11	---	
	9/12	5		2	---	
S-Micro (H6)	8/29	5		210*	---	
	9/'3	5		5	---	
	9/12	5		1	---	

*largely non-petroleum
aby GC/MS
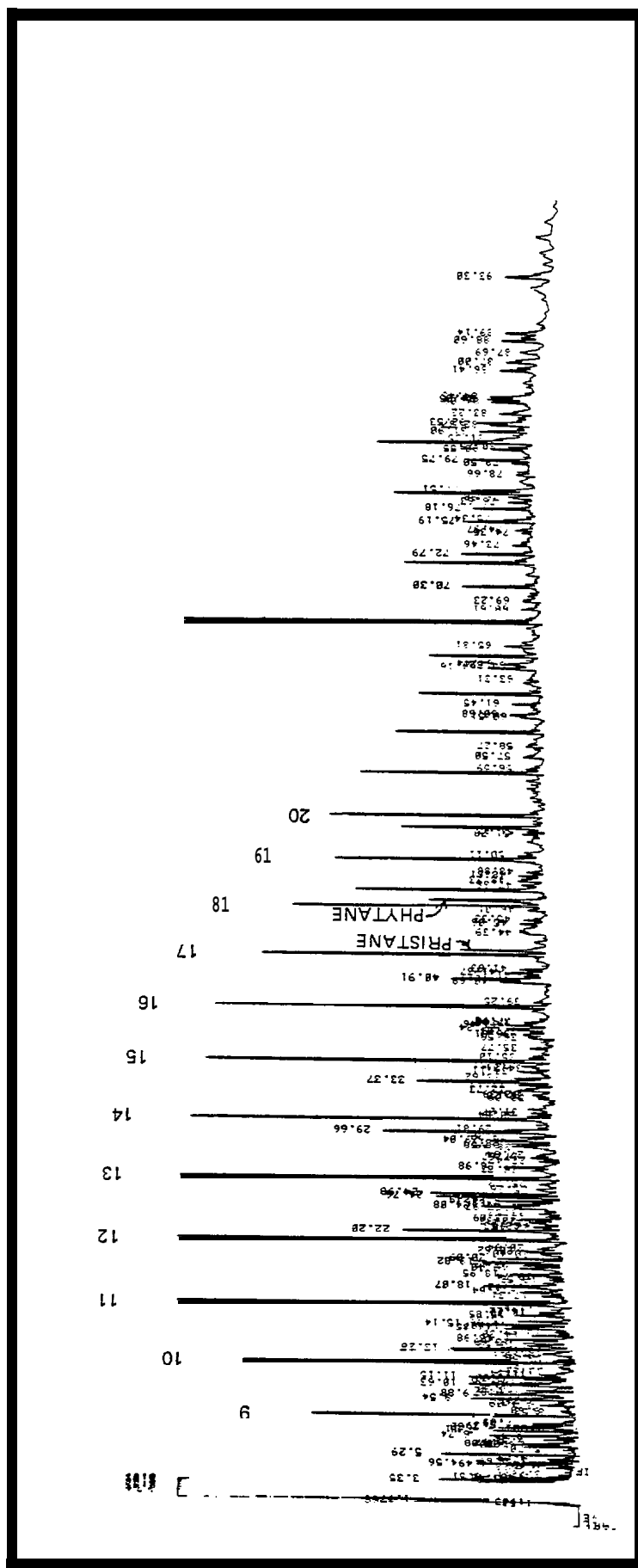
Figure 3.17. HMWHC (Saturates) Bay 9; N-Micro (8/29 - : Numbers   Peaks Represent
N-Alkane Carbon Numbers.
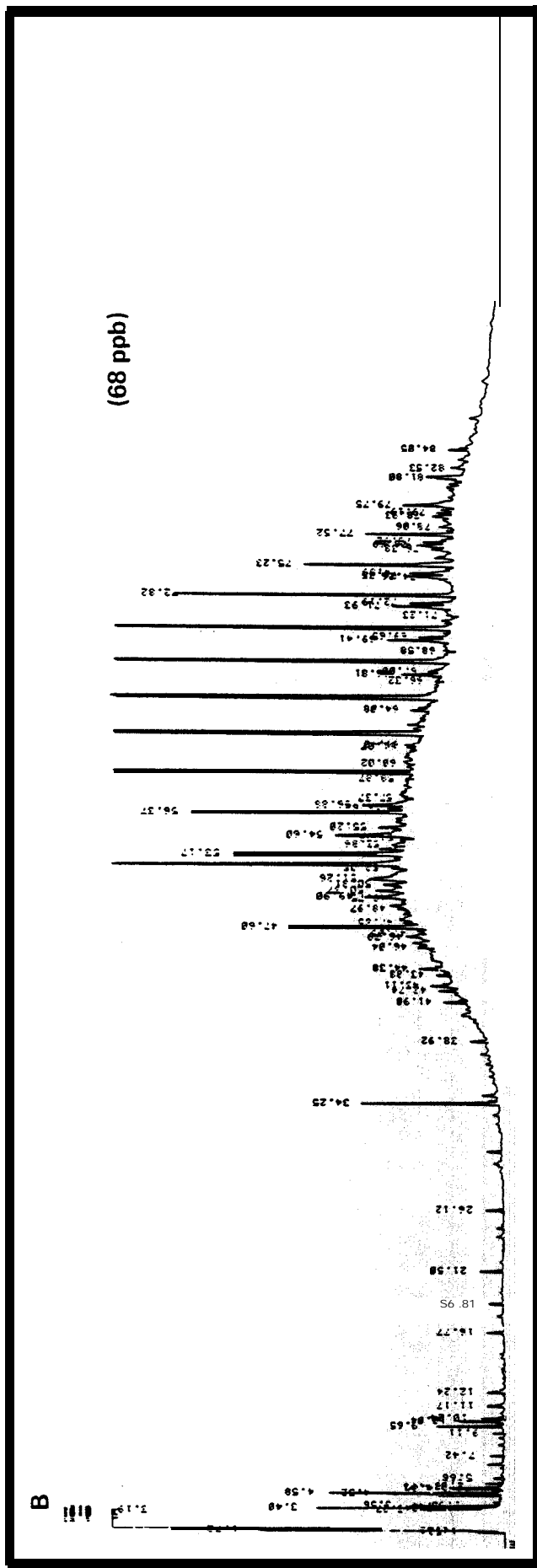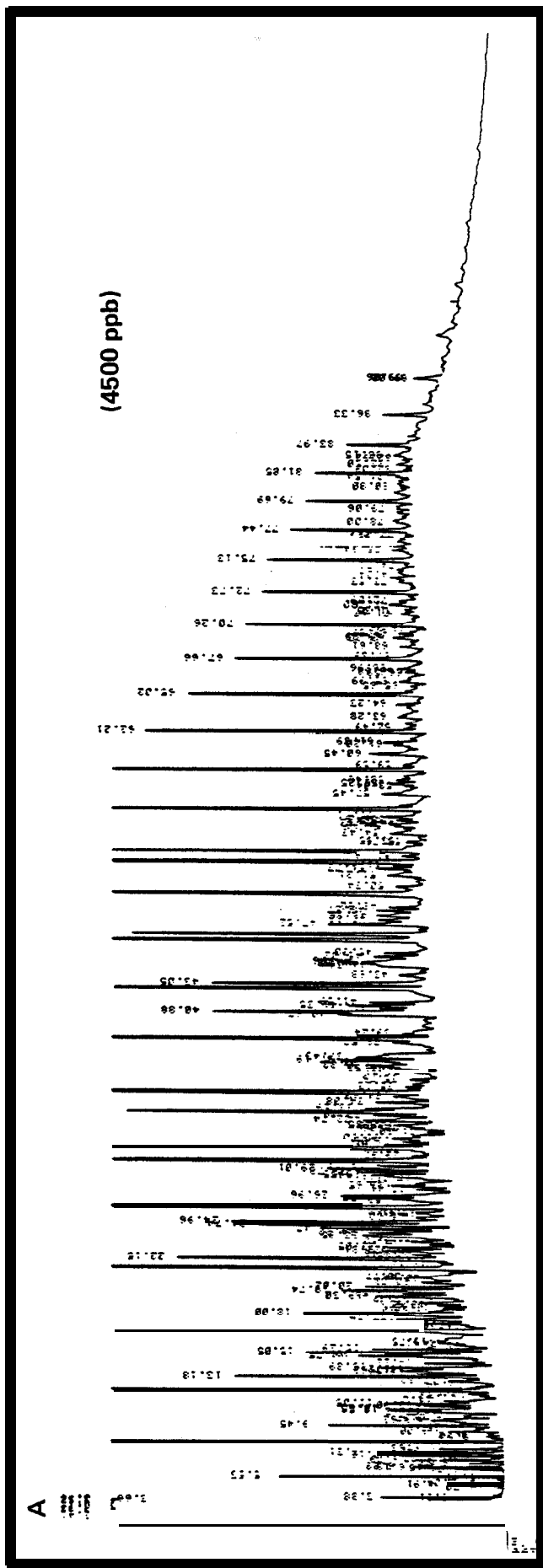
Figure 3.18. HMWHC, A—Baffin Queen (4 m); B—Baffin Queen (2 m); 2400 Hours (8/27)(Bay 9).

In general, the lower levels of oil seem to be characterized by greater weathering, perhaps implying a **physico-chemical** fractionation followed by differential movement of "dissolved" (colloidal) and particulate oil plumes. The longevity of oil of similar composition to that discharged may be attributed to either the long-term dispersant-mediated stabilization of discharged oil droplets or the coincidental movement of dissolved and particulate oil plumes, the former containing the lighter saturates and aromatics and the latter containing particulate depleted in these more easily weathered components, the combination of which give the appearance of unaltered oil. Such a difference is observed by comparing the GC^2 traces in Figures 3-19 and 3-20. The whole water samples taken from SS2 (10 m) at 2300 hours are more concentrated (2.8 ppm) substantially less weathered than one taken some 6 hours earlier at the BQ site (1.4 ppm) (note that there was no compositional difference at the BQ site at this time; Table 3-3). Therefore, one concludes that a dissolved oil plume characterized by light aromatics (Figure 3-19) and saturates coincides with the particulate plume in this "older" sample. Where differential movement of water and oil particle plumes occurs, the oil appears depleted in this dissolved material, such as that observed in samples with lower overall oil concentrations.

GC^2/**MS** analyses of several Bay 9 HMWHC samples have been performed to date as indicated in the **AWR** column in Table 3-3. Compositions of these samples are plotted in Figures 3-21 and 3-22. Of particular note is the fact that with the very high concentration levels (12-40 ppm) the AWR value is somewhat higher than in the **oil/dispersant** mixture (%3.5-5.5), indicating water column enrichment of light aromatics (e.g. , **naphthalenes, alkylated** benzenes) in these samples and

Saturates

n-C9   n-C17

n-C25

-J--‑--L-..L..

Aromatics

AB   N

N = Naphthalenes (C_1, C_2, C3, C4)

Alkylated
DBT, P
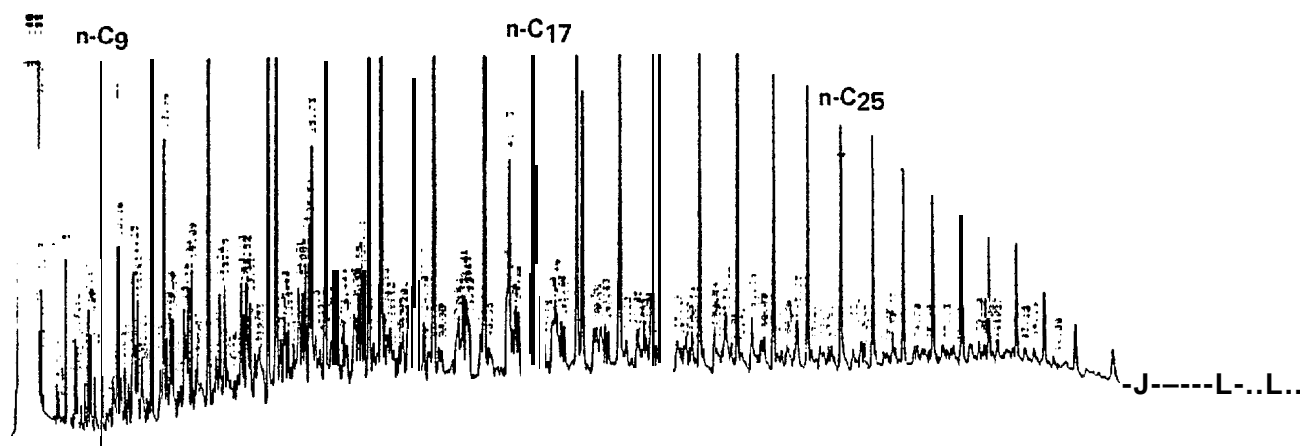
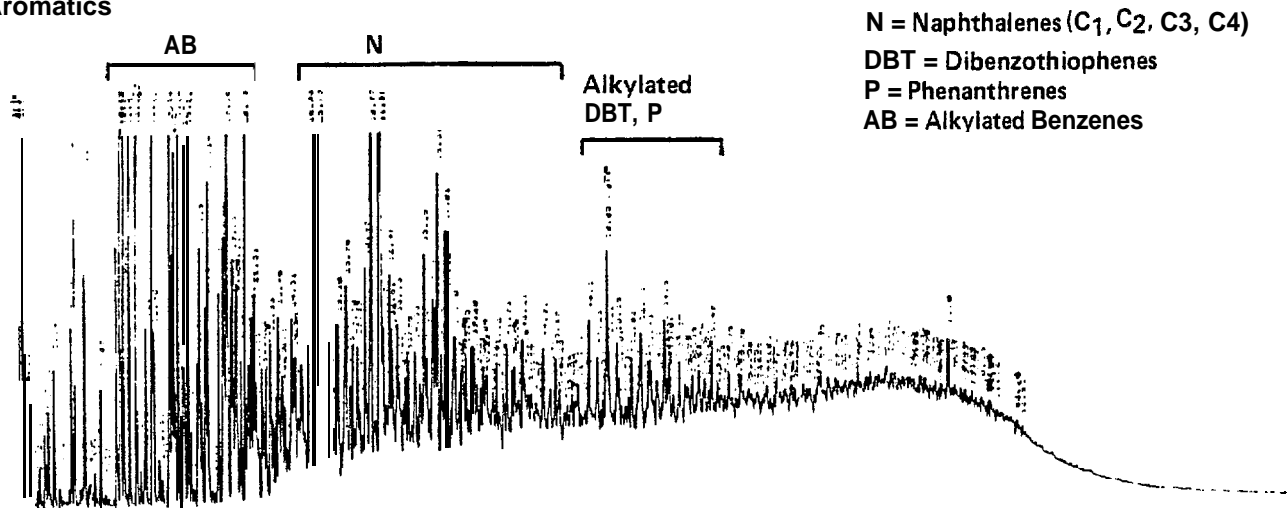DBT = Dibenzothiophenes
P = Phenanthrenes
AB = Alkylated Benzenes

Figure 3.19. HMWHC, Whole Water, SS2 10 m, 2300 Hours, (8/27)(Bay 9).
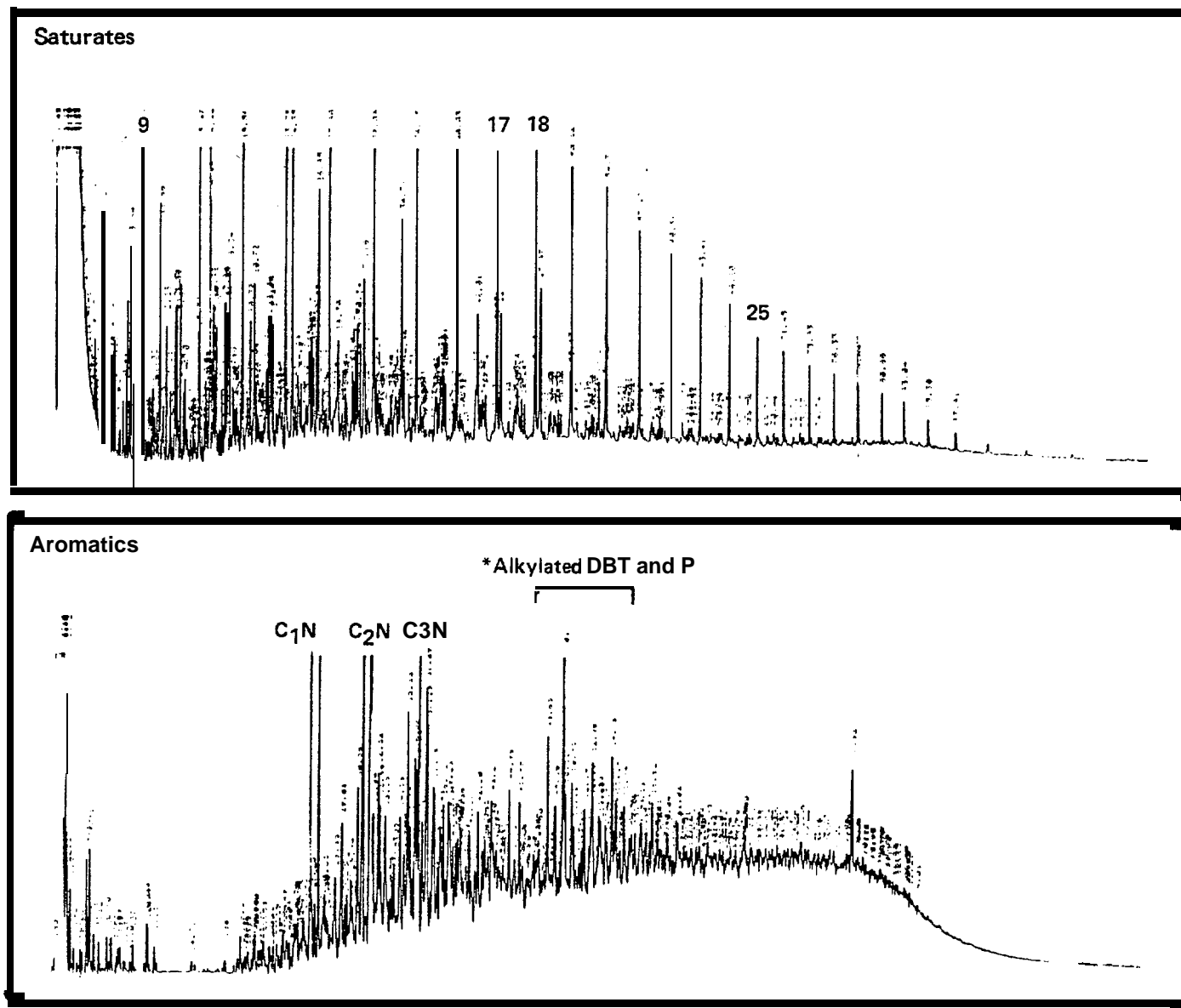
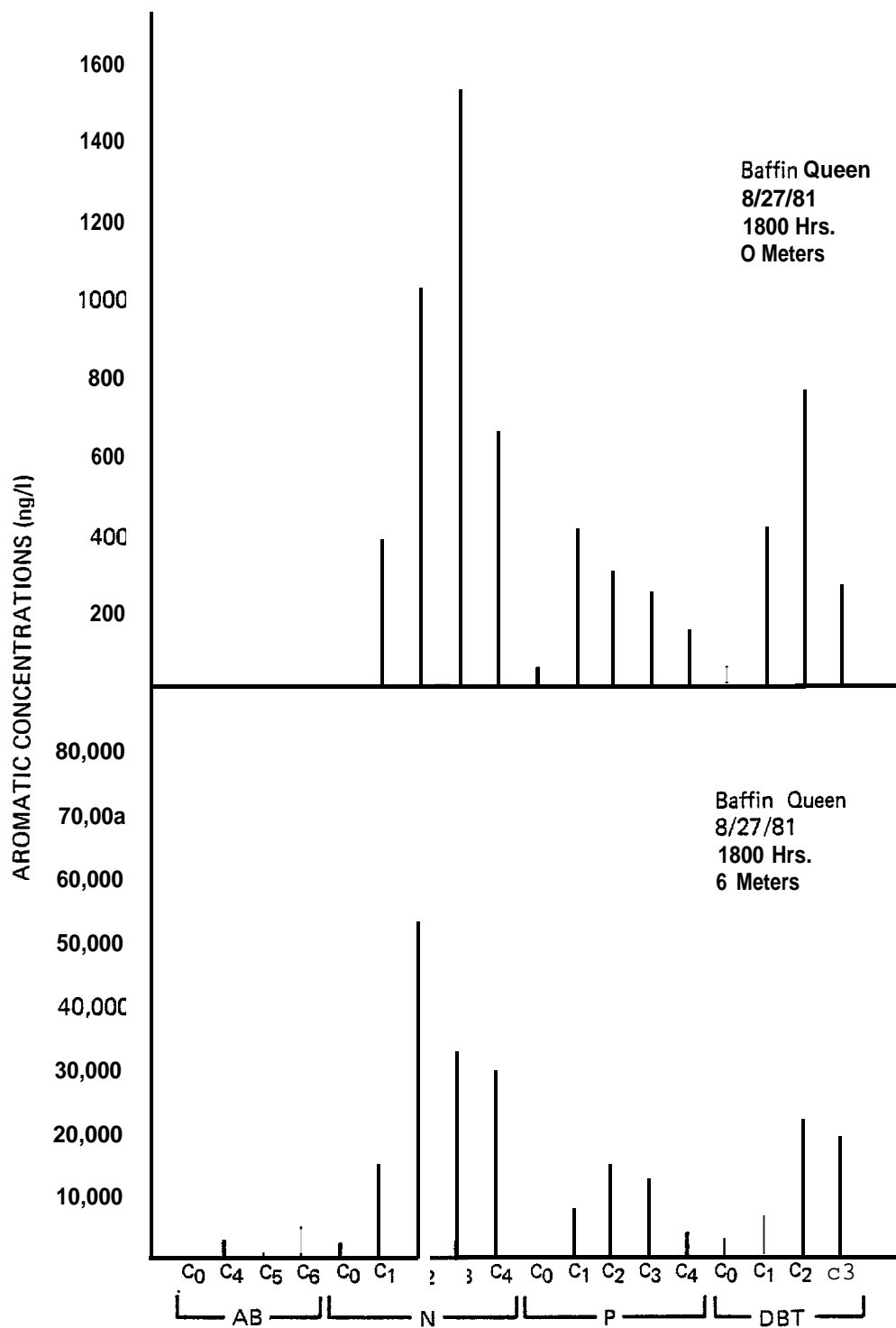**Figure 3.20. HMWHC,** Whole Water, Baffin Queen, O m, 1800 Hours, (8/27)(Bay 9).

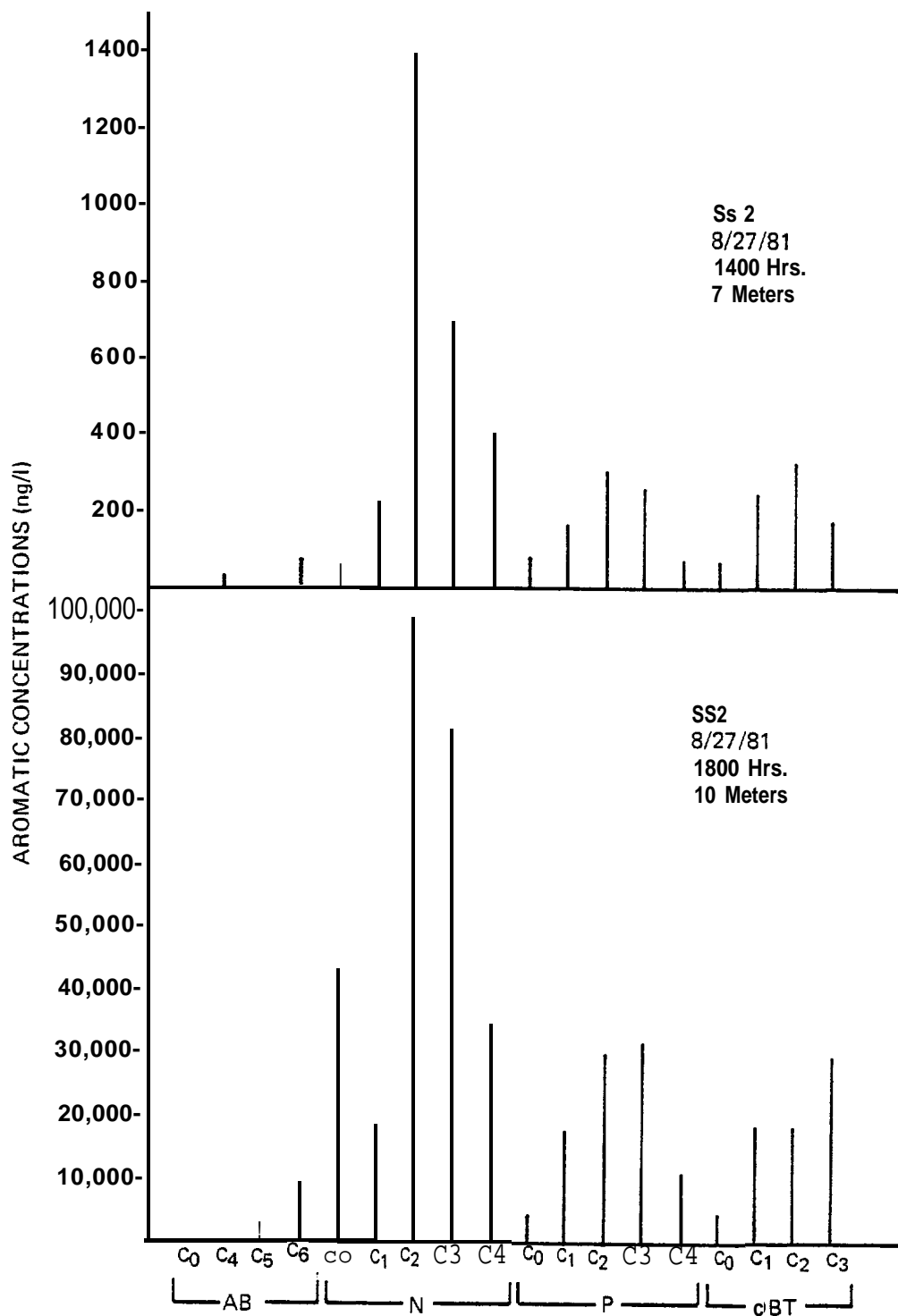Figure 3.21. Aromatic hydrocarbons in HMWHC samples (Bay 9).

Figure 3.22. **Aromatic hydrocarbons in** HMWHC samples **(Bay** 9).

implying an enrichment of dissolved components in the sub-
surface plume of dispersed oil. The levels of naphthalene
are observed to be as high as 45 µg/l, methyl naphthalenes
as high as 100 µg/l, dimethyl naphthalenes as high as 210
µg/l and alkyl benzenes as high as 40 µg/l in the water
column samples. More commonly, the range of these toxic
aromatic compound concentrates are 1-50 ppb (µg/l) during
the discharge.

The longer term nature of aromatic hydrocarbon concentra-
tions are revealed in the HMWHC (large volume) samples (see
Section 3.1.2.3).

3.1.2.2b Bay 10

Concentrations of oil in the water column of Bay 10
were lower than those for Bay 9, but reflected the same
concentration and compositional trends. The highest instan-
taneous concentration observed in Bay 10, 2.8 ppm (see
Table 3-4 and Figure 3-23), was at the S-micro station at
∿4 m depth at 0100 hours on August 28. It has been shown
(Volume 1) that oil had entered Bay 10 earlier than this
time by direct northern transport of dispersed oil. Indeed,
Green et al. (1982) showed that ∿1 ppm of oil was found
at 6 meters depth in Bay 10 at 1530 hours on August 28.

Compositionally we again find that oil "parcels" of low
to medium concentration levels (10-300 ppb) are more highly
weathered than oil at higher levels (>1000 ppb) even though
the latter oil may have been in the system for a longer period
of time. This is again evidence for the coherent movement of
particulate oil, dissolved oil, and seawater with the differ-
ent physical-chemical forms of oil moving together with little

TABLE 3-4

BAY 10 HMWHC DATA - WATER

STATION	DAT E	DEPTH (m)	TIME	CONC. (μg/L)	SHWR
BQ (Baffin Queen)	8/28	6.5	1300	2.3	1.0
N-Micro (H3)	8/21	9-1o	2300	2.6	---
		2-4	2300	1.3	---
		6-8	2300	1.7	---
	8/27	9-1o	2000	100	2.0
	8/28	o-2	0200	151	1.9
		7-8	1400	570	2.1
		9-1o	0200	17	1.5
	8/29	5		58	1.7
	9/5	5		16	---
	9/12	5		18	---
S-Micro (H4)	8/29	9-10	1600	250	2.0
	9/3	3-4	0100	2820	2.6
	9/'12	9-10	0100	340	1.2
	8/29	5		86	2.2
	9/5	5		16	---
	9/12	5		3	---
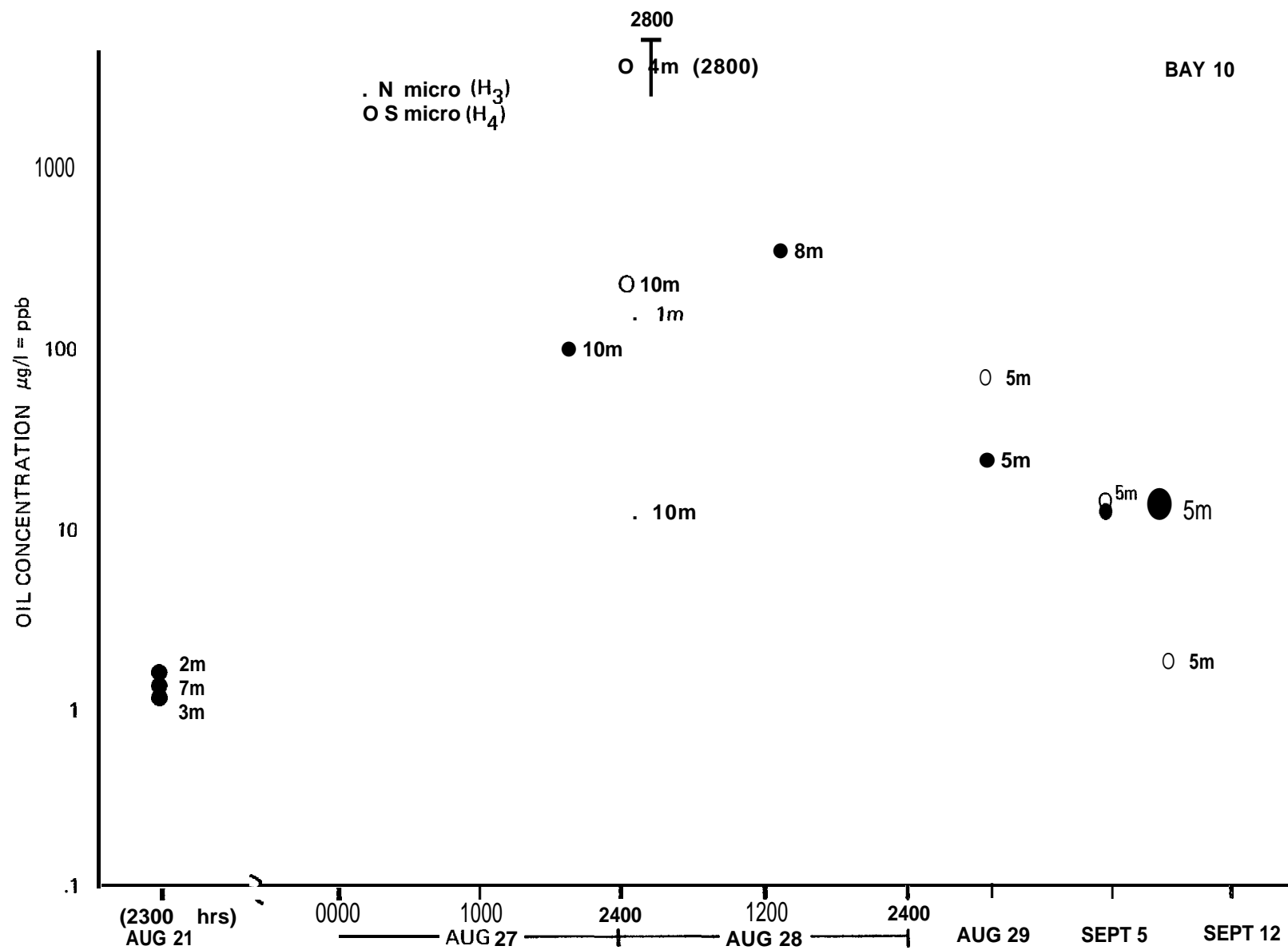
Figure 3.23. Concentrations in Bay 10 Waters (Micro Stations), as Determined by GC^2.

mixing, thus preserving higher concentrations of "fresher" oil. Indeed, the 4 m parcel of oil reaching the S-micro station at 0100 hours on August 28 is quite fresh in spite of its presumed circuitous movement from the diffuser, first southerly and then northerly, passing through Bay 9 and into Bay 10. It is interesting to note that this "preserved" oil layer overlies an older, more weathered, and **chromato-**graphically altered oil at 9-10 meters.

3.1.2.2c Bay 7

The only water samples available to this program from Bay 11 were those microbiology station samples at N-micro (H7) and S-micro (H8) commencing on September 3, or nearly one week after the dispersed oil spill. These concentrations (Table 3-5) indicate that very low levels of petroleum were observed.

The GC^2 profiles revealed hydrocarbon compositions resembling small amounts of petroleum combined with larger amounts of biogenic material. Concentrations in Table 3-5 reflect mainly the **biogenic** part of the GC^2 trace comprised of small amounts of substantially weathered (SHWR=1.1-1.4) oil.

3.1.2.2d Bay 11

HMWHC measurements were made at four different locations at Bay 11, from August 19 through September 3, and at three other locations from August 22 to September 12. Concentrations during this time ranged from no detectable oil (less than 0.5 **ppb**) to 730 ppb (Table 3-6; Figure 3-24). The

TABLE 3-5

BAY 7 HMWHC DATA - WATER

STATION	DEPTH	DATE	CONCENTRATION (μg/l)	SHWR
N-Micro	5	9/3	5 (48)[a]	1.4
		9/12	2 (4)	---
S-Micro	5	9/3	5 (1o)	1.2
		9/12	4 (8)	1.1

[a]Numbers in parentheses represent total "hydrocarbons" in GC^2 trace; unbracketed number is estimated petroleum content of samples.

TABLE 3-6

BAY 11 HMWHC DATA - WATER

STAT 10N	DATE	TIME	CONC. (µg/L)	SHWR	AWRa
SS-1 (3m, bottom)	8/19	1700	less than 0.5 ---		
		2000	less than 0.5 ---		
	8/21	0900	6.4	1.2	
SS-2 (3m, bot tom)	8/19	1700	1.1	2.3	
		2100	8.4	1.1	
	8/20	1600	4.3	1.0	
		1700	5.5	1.2	
	8/21	0900	2.0	3.5	
N-boom (O-2 m)	8/19	1500	0.5	1.0	
		1700	5.9	1.4	4.6
		1800	0.5	1.1	
		2100	140	1.6	31
	8/20	1700	730	1.0	
S-boom (O-2 m)	8/20	1700	7.4	1.3	
Mid-boom (O-2 m)	8/22	1600	720	2.3	5.8
N-micro (Hi, 5 m)	8/29	--	63	1.6	3.2
	9/5		29	---	---
	9/12		4	---	1500
S-micro (H2, 5 m)	8/29	--	61	2.0	3.1
	9/5		410b	---	1500
	9/12		6	---	---

a From GC^2/MS data.
bLargely nonpetroleum.

Figure 3.24. Concentrations of Oi in Bay 11 Waters as Determined by GC[2].

highest concentration was observed in two samples of surface
water. Note that while the concentrations are the same, the
mid-boom (8/22) sample contained very fresh oil (Figure 3-25;
SHWR=2.3), and the N-boom sample (8/22) contained a weathered
oil (Figure 3-26; SHWR=1.0) and an anomalous aromatic GC^2
profile. Neither sample was microbially altered as is
evidenced from the high ALK/ISO ratios in these samples (4.4
and 3.7 respectively).

GC^2 profiles transformed into SHWR data (Table 3-6)
indicate a highly variable degree of weathering of oil cap-
tured in water column samples.

Concentrations at the microbiology stations Hl and H2
determined from August 29 reveal significant concentrations
of oil, ~60 ppb on the 29th, which could have resulted from
intrusion of dispersed oil (Bay 9,10) or from leaching off of
the Bay 11 beach. GC^2/MS results (Figures 3-27 A,B, 3-28)
are most revealing in that water-borne oil from August 29
consisted of more or less whole "fresh oil" (AWR = 3.1) while
only a dissolved fraction, abundant in naphthalene, methyl
naphthalene and alkyl benzenes were detected on September 5
and 12 (AWR = 1500, see Table 3-6).

The lack of samples taken between August 22 and 29
precludes any speculation on trends in Bay 11 water column
concentrations prior to the dispersed oil spill. The presence
of whole oil in the water (60 ppb) on August 29 implies some
Bay 10 to Bay 11 cross-contamination.

Note that the 410 ppb value (S-micro, Sept. 5; Table 3-6)
corresponds to a largely non-petroleum component distribution
(see Figure 3-29). The relationship of this GC^2 distribution
with that in Corexit 9527 is being investigated.

Figure 3.25. Hydrocarbon Composition of Bay 11 MID Boom (8/22) Water Sample.
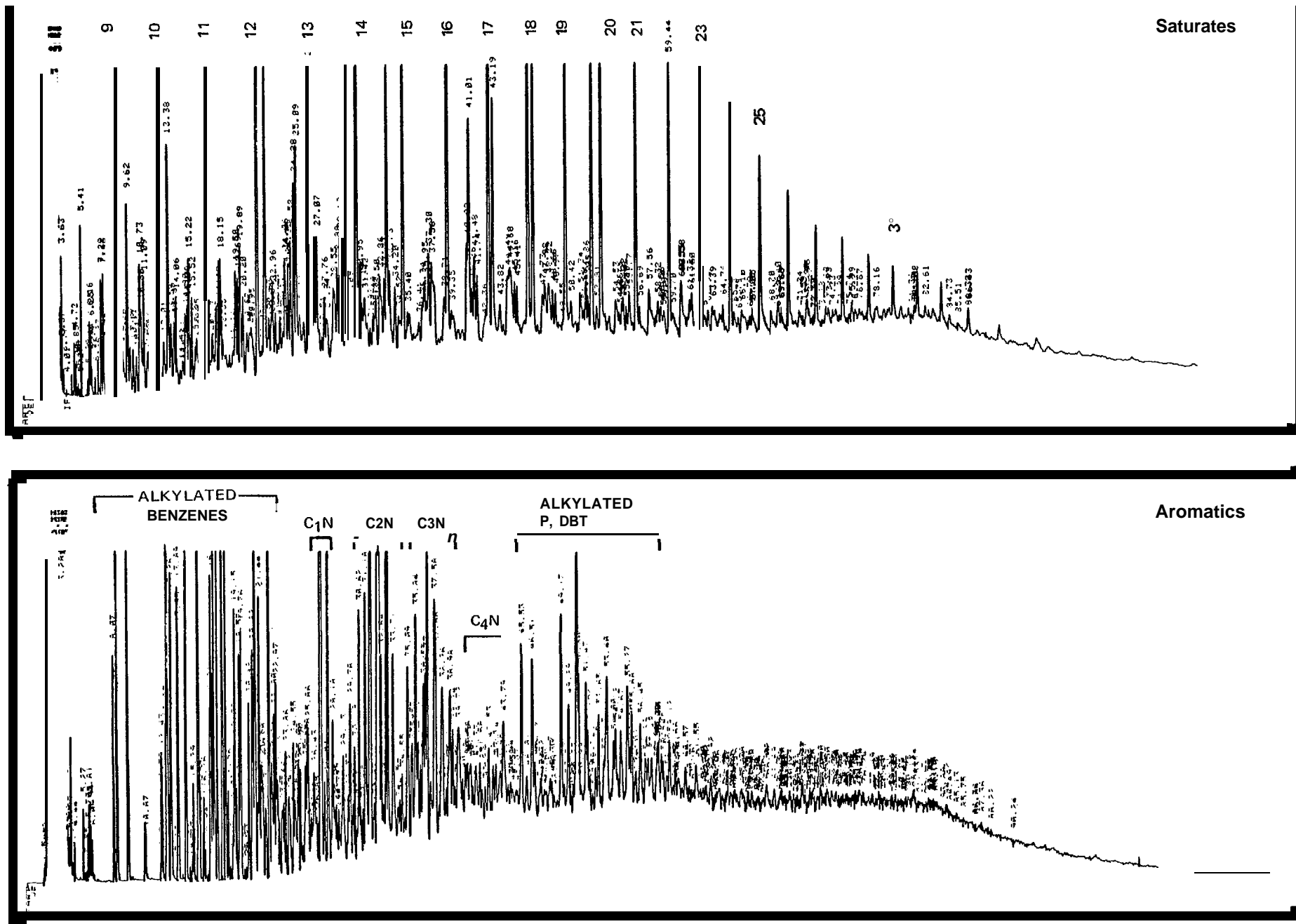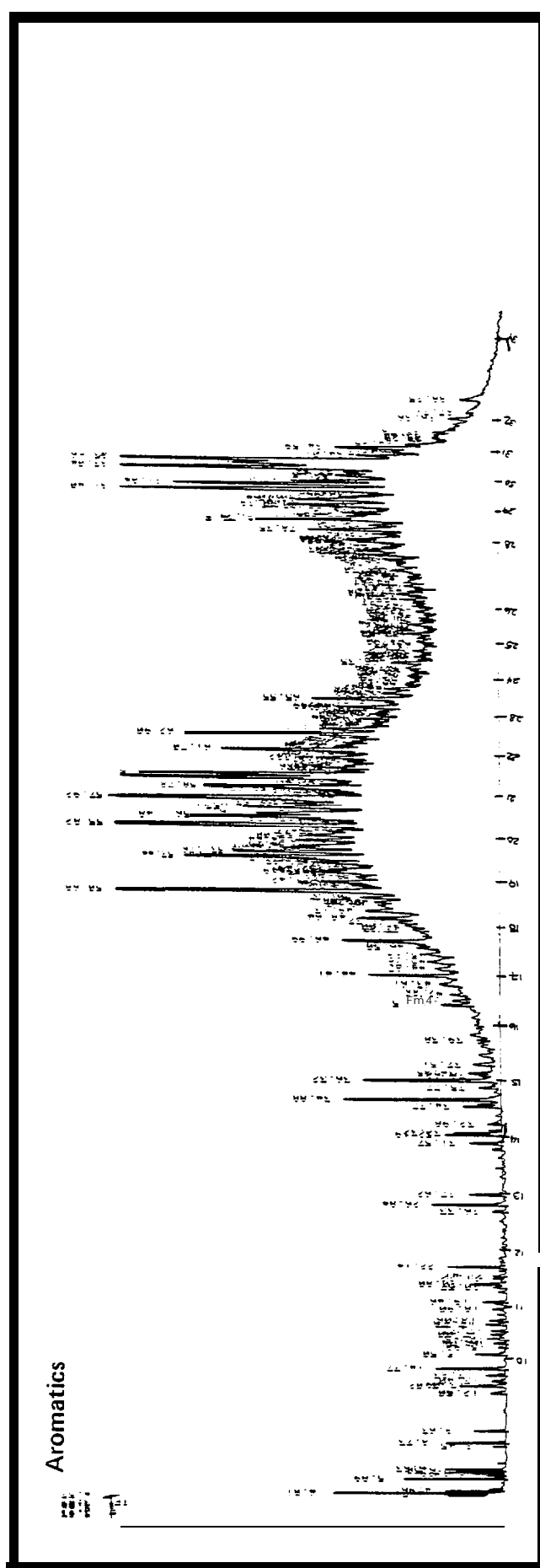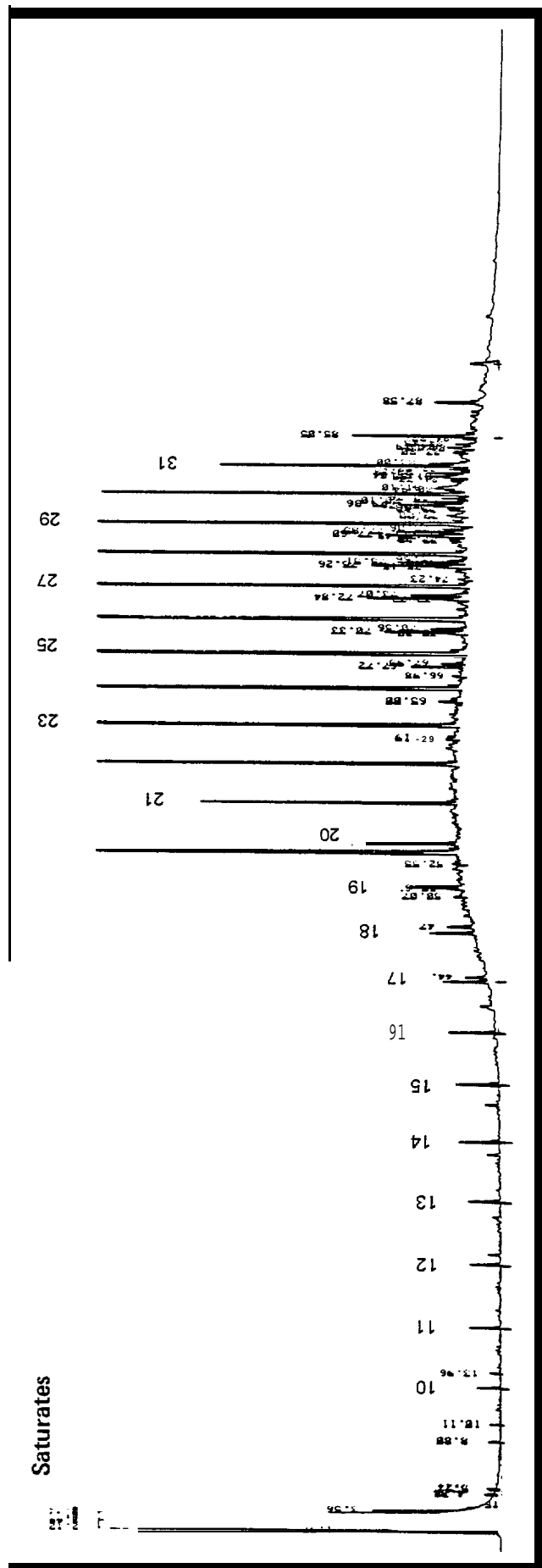
Figure 3.26. Hydrocarbon Composition of N Boom—Bay (8/22) Water Sample.

Figure 3.27. Aromatic hydrocarbon profiles of HMWHC water **samples from Bay 11 microbiology plots.**
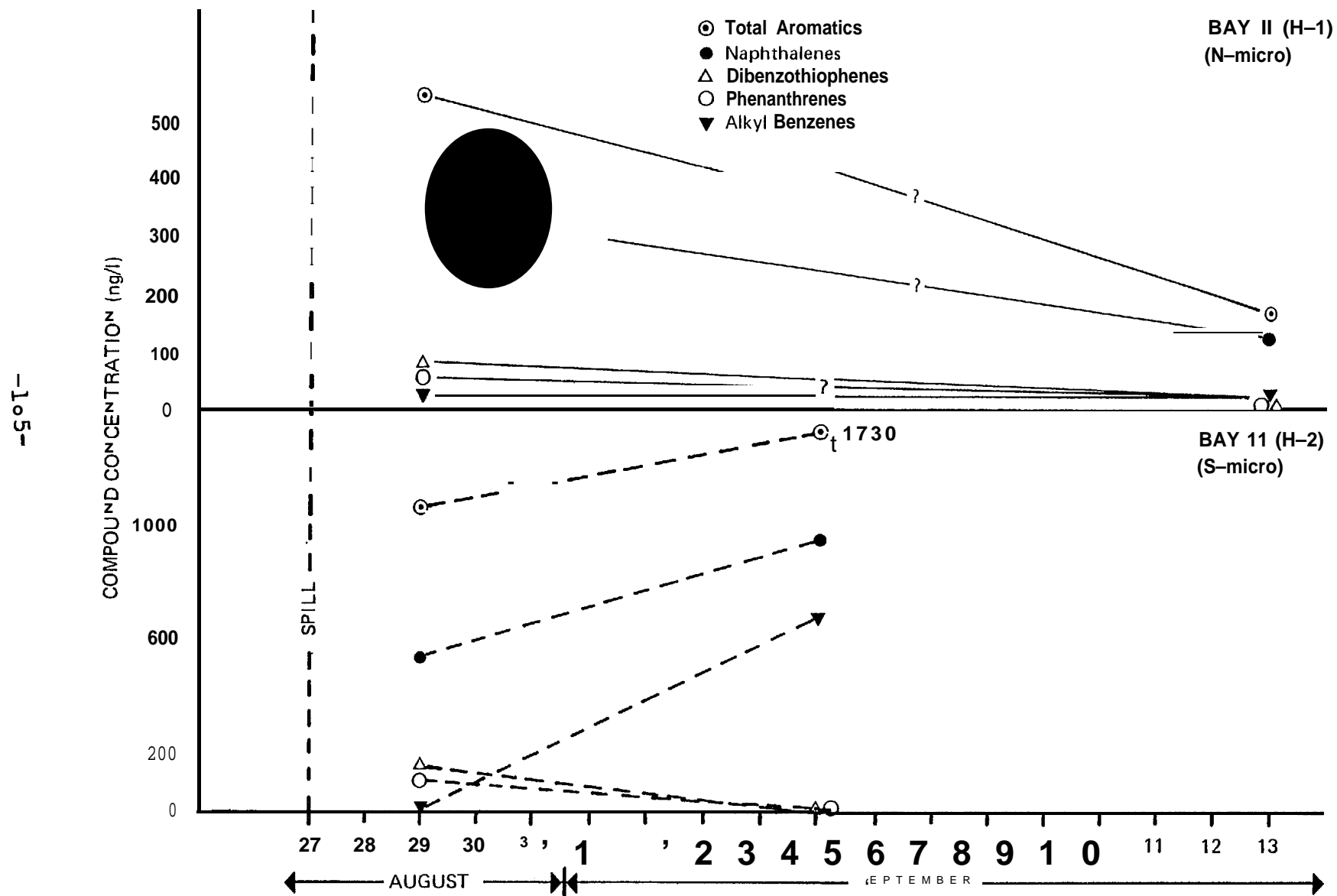
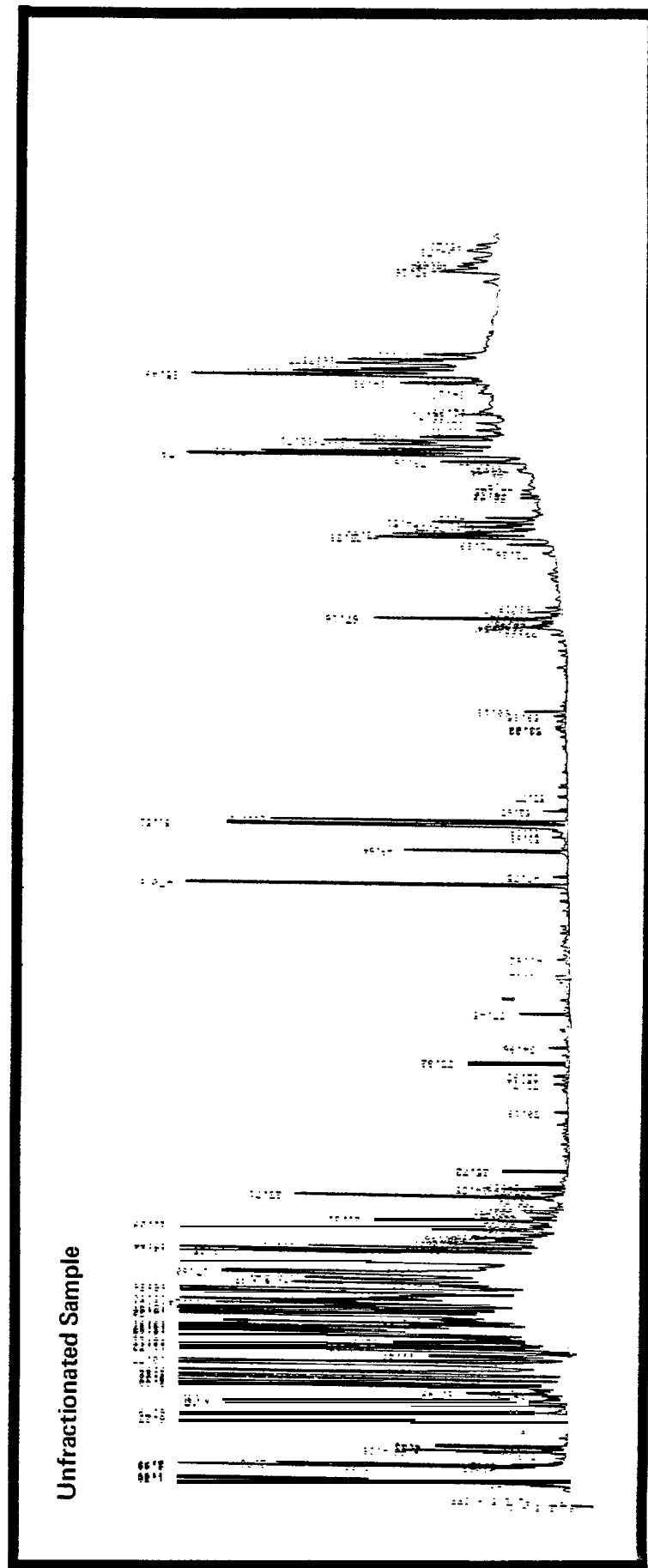Figure 3.28. Plot of Trends in Aromatic composition of Bay 11 Water Samples.

Figure 3.29. Anomalous Composition of Water Samples from Bay 11 (H₂); (9/15).

Much of the available fluorescence data indicate that oil
was largely confined to the top meter of the water column of
Bay 11 and that **bottom water at 3 m** depth contained no oil.
GC2 data (Table 3-6) confirm the presence of large quantities
of oil (700-1000 ppb) in surface waters, but owing to the
lower detection limits of the GC2 method, low levels of oil
were detected in bottom waters.

3.1.2.3 High Molecular Weight Hydrocarbons
(Large-Volume Samples)

The large-volume water samples consisted of two parts:
(1) a filter upon which particulate hydrocarbons were obtained
and (2) a polyurethane plug located "downstream" of the
filter, upon which "dissolved" hydrocarbons which passed
through the filter were obtained.

3.1.2.3a Bay 9

Samples were obtained during the period August 13 to
September 5, 1981 from this bay. The highest concentrations
observed were in the particulate fraction of the first sample
taken after the spill (1.5 days after the spill on August 29).
Concentrations of particulate oil were observed to be 22 ppb
(=μg/L) at 2 meters depth. (Due to the uncertainty as to the
volumes of water actually processed, these concentrations
should be considered to represent minimum values. The data
set is valuable in ascertaining the presence of oil in the
water column and in revealing its composition.) These levels
(Table 3-7) are similar to those observed two days later
(August 3; 18 ppb) at 6 meters depth. Thereafter levels
decreased (see Figure 3-30), but moderately weathered petro-
leum was detected on September 5. Concentrations in the

TABLE 3-7

HIGH MOLECULAR WEIGHT HYDROCARBONS IN LARGE VOLUME SAMPLES

BAY	DATE	DEPTH	FILTERS (PARTICULATE OIL)				PLUG ("DISSOLVED OIL")			
			NOMINAL OIL CONC. (µg/L)	SHWR	AWR[a]	GC TYPE	NOMINAL OIL CONC. (µg/L)	SHWR	AWR[a]	GC TYPE
9	Aug 13	5	0.2	---	---	C/B	0.2	---	---	HO
	27		------------------------ S	P	I	L L	----------------------			-------
	29	2	22.0	1.8	1.0	FO	0.8	1.1	1.7	WSF
	31	6	18.0	1.5	---	MO	1.8	---	---	WSF
	Sept 2	6	2.5	1.4	---	MO	0.7	---	---	WSF
	5	6	0.7	1.4	---	MO	0.3	---	---	WSF
10	Aug 14	5	0.2	---	---	C/B	0.1	---	---	HO
	18	5	0.2	---	---	C/B	0.05	---	---	C/B
	23	3	0.2	---	---	C/B	0.05	---	---	C/B
	27		-------- ------- --------- S	P	I L L		----------------------			-------
	28	4	30.0	1.7	---	FO	4.6	1.8	2.3	FO
	30	6	21.0	1.3	1.0	MO	2.9	1.9	1.5	FO/WSF
	Sept 4	6	0.2	---	---	C/B	1.5	1.9	---	FO
7	Aug 27	2	1.9	1.1	---	HO/B	0.7	1.1	---	HO
	29	2	1.0	1.2	---	HO/B	2.2	1.7	---	HO/WSF
	Sept 6	6	0.2	---	---	C/B	0.1	1.1	---	HO
11	Aug 12	4	0.5	---	---	C/B	0.2	---	---	HO
			-------------------------- S P I L L #1				------- -------------			----
	19	3	5.9	1.9	---	FO/B	less than 0.05	---	---	C/B
	20	1	10.2	1.7	1.4	FO/B	0.5	1.0	---	HO
	21	1	2.0	1.3	---	HO/B	0.05	---	---	C/B
	22	1	3.5	1.6	---	MO/B	0.3	1.0	1.6	WSF
	22	6	0.6	1.5	---	MO/B	4.7	1.0	---	WSF
	24	6	0.9	1.4	---	MO/B	0.2	1.0	---	WSF
	25	1	2.2	1.5	---	MO/B	0.6	1.0	---	HO/WSF
	25	6	0.9	1.2	---	HO/B	0.4	1.0	---	HO
			-------------------- ------- S P I L L #2				------------- -------			----
	Sept 3	6	1.3	1.2	---	HO/B	0.05	---	---	C/B

[a]Data by GC^2/MS.

KEY : GC TYPE
FO : "fresh" oil
MO : oil with moderate weathering (SHWR 1.5-1.7)
HO: oil with heavy weathering (SHWR less than 1.4)
WSF: water soluble fraction of oil (mainly aromatics)
B: biogenic compounds
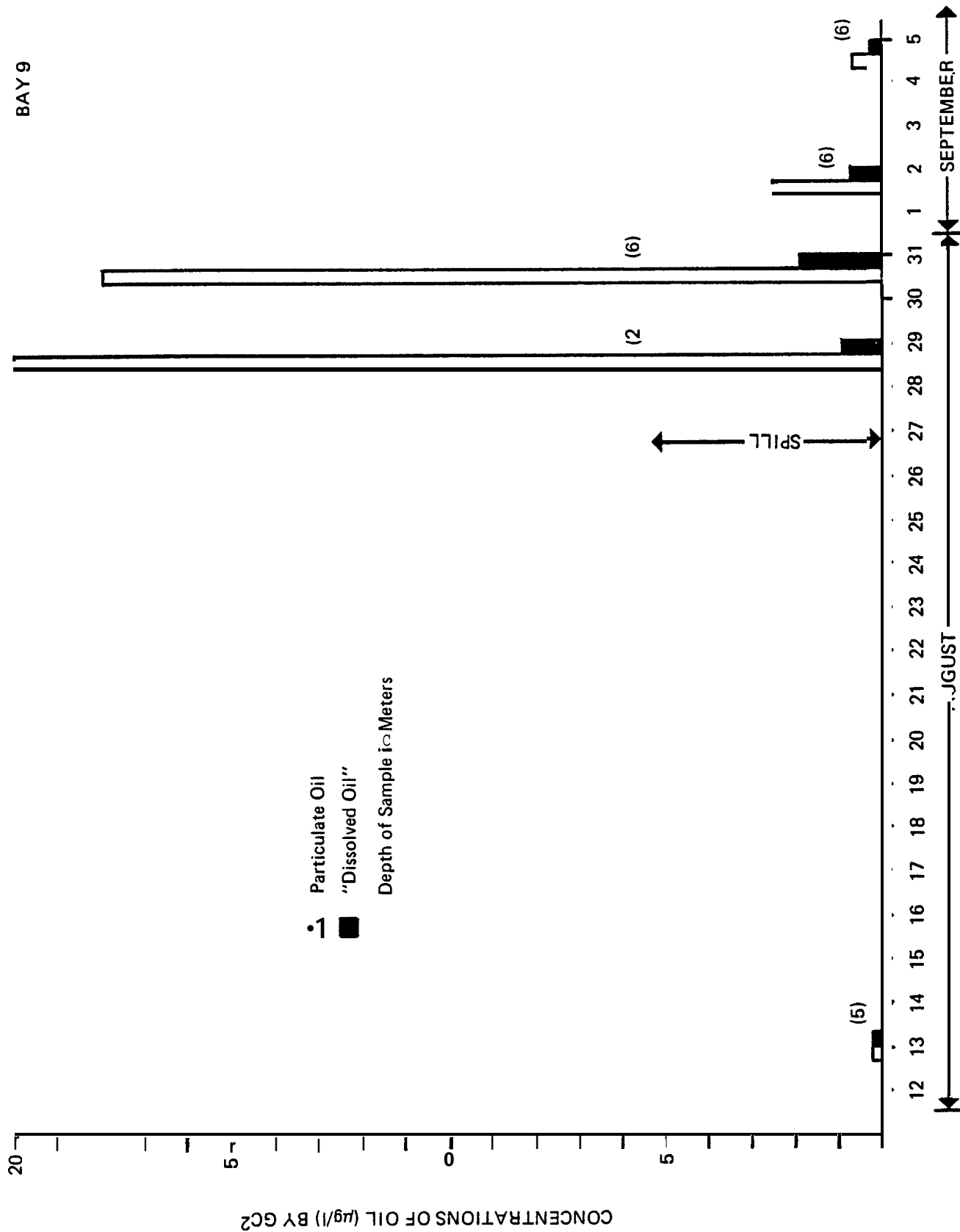c: clean GC trace with respect to petroleum

Figure 3.30. Large Volume Water Sample Concentrations (Bay 9).

filterable of "dissolved" fractions of these samples was
considerably lower, never exceeding 1.8 ppb. Trends in
concentration data are graphed in Figure 3-30.

Compositions of petroleum residues in the two fractions
differed markedly. In general, the particulate oil residues
consisted of saturated hydrocarbons at various stages of
evaporative/dissolution weathering as defined by the SHWR.
With time, this saturated assemblage lost progressively more
of its C_{10}-C_{17} components (SHWR changing from 1.8 to 1.4).
The particulate samples contained only very small quantities
of aromatic hydrocarbons and only those associated with the
two-ringed compounds. Representative GC^2 traces are shown
in Figures 3-31 through 3-33. Where levels were moderate to
high, both the dissolved and particulate samples contain
whole oil. The dissolved fraction, though, contained much
less saturated material than did the particulate and
indications of water soluble aromatics (Figures 3-31 and
3-32). Saturated hydrocarbon composition of the particulate
fraction varied with time (Figure 3-33).

GC^2/MS results are presented in Table 3-8 and indicate
the presence of naphthalene compounds in the dissolved fraction
only and equal amounts of the other aromatics in both fractions.
That the overall abundance of hydrocarbons is greater in the
f_1 fraction indicates that this fraction is primarily of a
saturated hydrocarbon nature.

3.1.2.3b Bay 10

As in Bay 9, the pre-spill (dispersed oil) hydrocarbon
values in both the particulate and dissolved samples from
Bay 10 were on the order of 0.05 to 0.2 ppb, reflecting
biogenic material and low levels of material classified
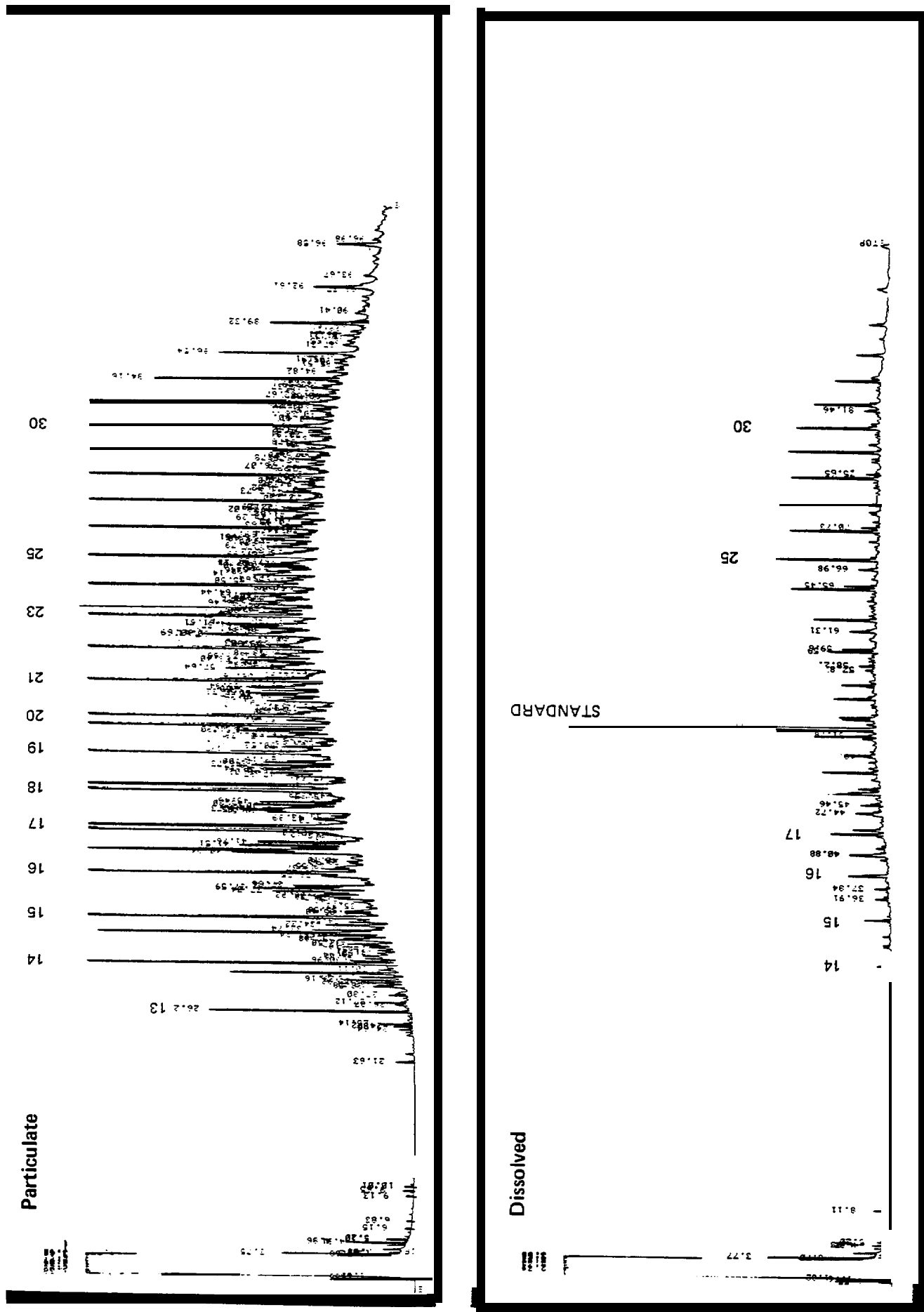
Figure 3.31. Large Volume HMWHC (Saturates) Bay 9 (8/29)(Numbers Refer to n-alkanes), (GC2 Composition).

Figure 3.32. Large Volume HMWHC (Aromatics) Bay 9 (8/29)(GC^2 Composition).

Particulate 9/2
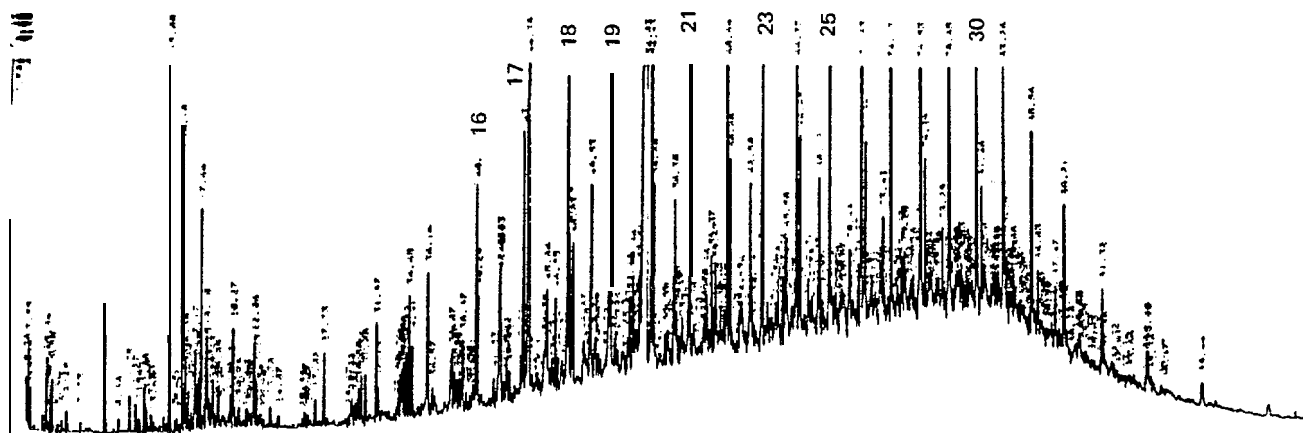
Particulate 9/5
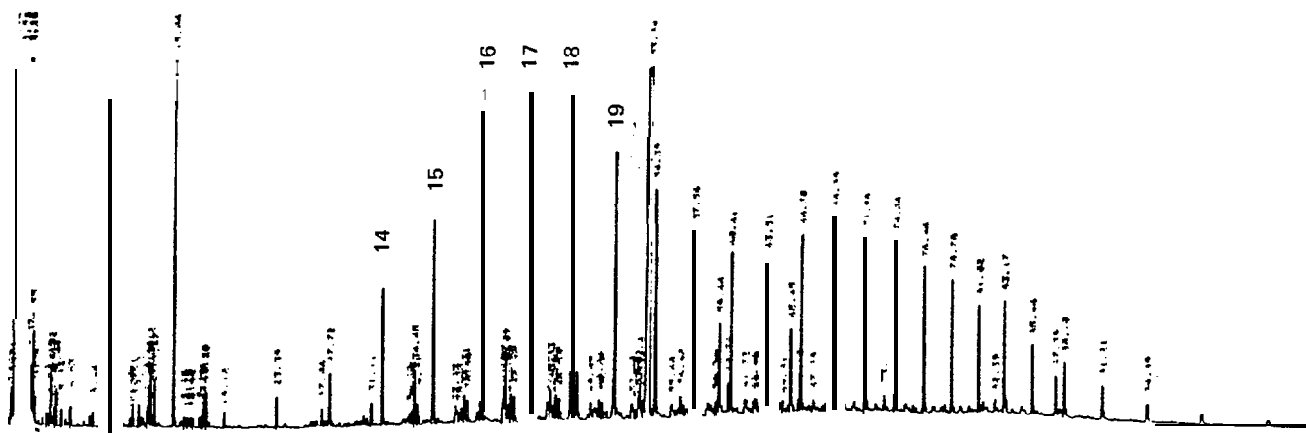
Figure 3.33. Large Volume HMWHC (Saturates) Bay 9 (GC^2 Composition).

TABLE 3-8

GC^2/MS RESULTS - LARGE VOLUME WATER SAMPLES (ng/l)

	BAY 9 - AUG. 29 2 METERS		BAY 10 - AUG. 30 6-METERS		BAY 10 - AUG. 28 4-METERS		BAY 11 - AUG. 22 6-METERS		BAY 11 - AUG. 20 1-METER	
	PARTICULATE	DISSOLVED	PART.	DISS.	PART.	DISS.	PART.	DISS.	PART.	DISS.
Alkyl benzenes	ND	ND	ND	ND		ND		ND	ND	ND
Naphthalene (N)		---	---	---		---		-- .	---	
C_1N	- --	1.3	---	---		53		---	- --	
C_2N	---	1.7	---	---		90		---	2.0	
C3N	---	3.3	---	2.5		110		1.0	6.0	
C4N	- - -	2.4	- - -	4.1		25		2.5	5.4	
ΣN	ND	8.7	ND	6.6		278		3.5	13.4	
Fluorenes (F)	---	---	---	---		6.0		---	---	
C_1F	---	---	---	1.1		23		---	---	
C_2F	---	---	---	3.1		40		2.1	1.6	
C3F	---	---	---	3.3		8.4		6.1	3.6	
ΣF	ND	ND	ND	7.5		77		8.2	5.2	
Dibenzothiphenes (DBT)	---	---	---	---		8		---	---	
C_1DBT	-- .	---	---	4.1		40		1.0	1.9	
C_2DBT	---	---	---	6.1		50		1.0	4.8	
C3DBT	1.7	1.2	---	3.8		10		2.1	5.7	
ΣDBT	1.7	1.2	ND	14.0		108		4.1	12.4	
Phenanthrene (P)	---	---	1.1	1.8		24		---	1.1	
C_1P	---	1.1	1.0	4.7		69		2.6	4.9	
C_2P	1.1	1.2	2.7	4.1		60		2.8	13	
C3P	2.0	3.0	---	2.8		8.8		4.7	15	
C4P	1.2	1.0	---	---		---		3.0	6.1	
ΣP	4.3	6.3	4.8	13.4		162		13.1	40.1	
ΣN+F+DBT+P	6.0	16.2	4.8	41.5		625		28.9	71.1	
AWR	1.0	1.7	1.0	1.5		2.3		1.6	1.4	

(Table 3-7) as **highly** weathered petroleum. This may **represent** low levels of actual background **petrogenic** material, as has been previously determined (**Boehm** 1981a) or may be related to insignificant but detectable levels of sampling contamination. Levels in Bay 10, obtained after the Bay 11 spill (August 19), do not indicate any movement of oil out of Bay 11 into the adjacent bays. Bay 10 water levels, of course, increase to 30 ppb (particulate) and 4.6 ppb (dissolved) after the dispersed oil spill in Bay 9 (August 27). Levels hold constant ($\sim$20 ppb [particulate], 2.9 ppb [dissolved]) through August 30. However, levels of the dissolved hydrocarbons are more significant in these Bay 10 samples than was observed in Bay 9, with dissolved levels in Bay 10 approximately 15 percent of the particulate values (see Table 3-7 and Figure 3-34). Rather than consisting of just the water soluble aromatics, the Bay 10 "dissolved" fractions (August 28) contained altered "fresh oil" with a complete suite of aromatics (Figure 3-35) and a skewed saturate distribution compared with the oil itself. The September 4 sample is quite interesting because although no particulate oil was found, low (1.5 ppb) levels of oil (Figure 3-34) were found on the plugs (i.e., filterable). Whether this material is **truly** dissolved or whether **submicron**-sized oil particles have passed the filter yielding a GC2 profile in Figure 3-36B is not known.

GC^2/**MS-derived** aromatic hydrocarbon results are presented in Table 3-8. The results, coupled with the gross concentration information in Table 3-7, confirm that most of the light aromatic hydrocarbons reside in the dissolved (or colloidal) state (AWR = 1.5-2.3), while the more concentrated f_1 fraction contains primarily saturated hydrocarbons. The Bay 10 August 28 sample contains a total of 4.6 ppb of oil of which 0.6 ppb is aromatic hydrocarbon material.
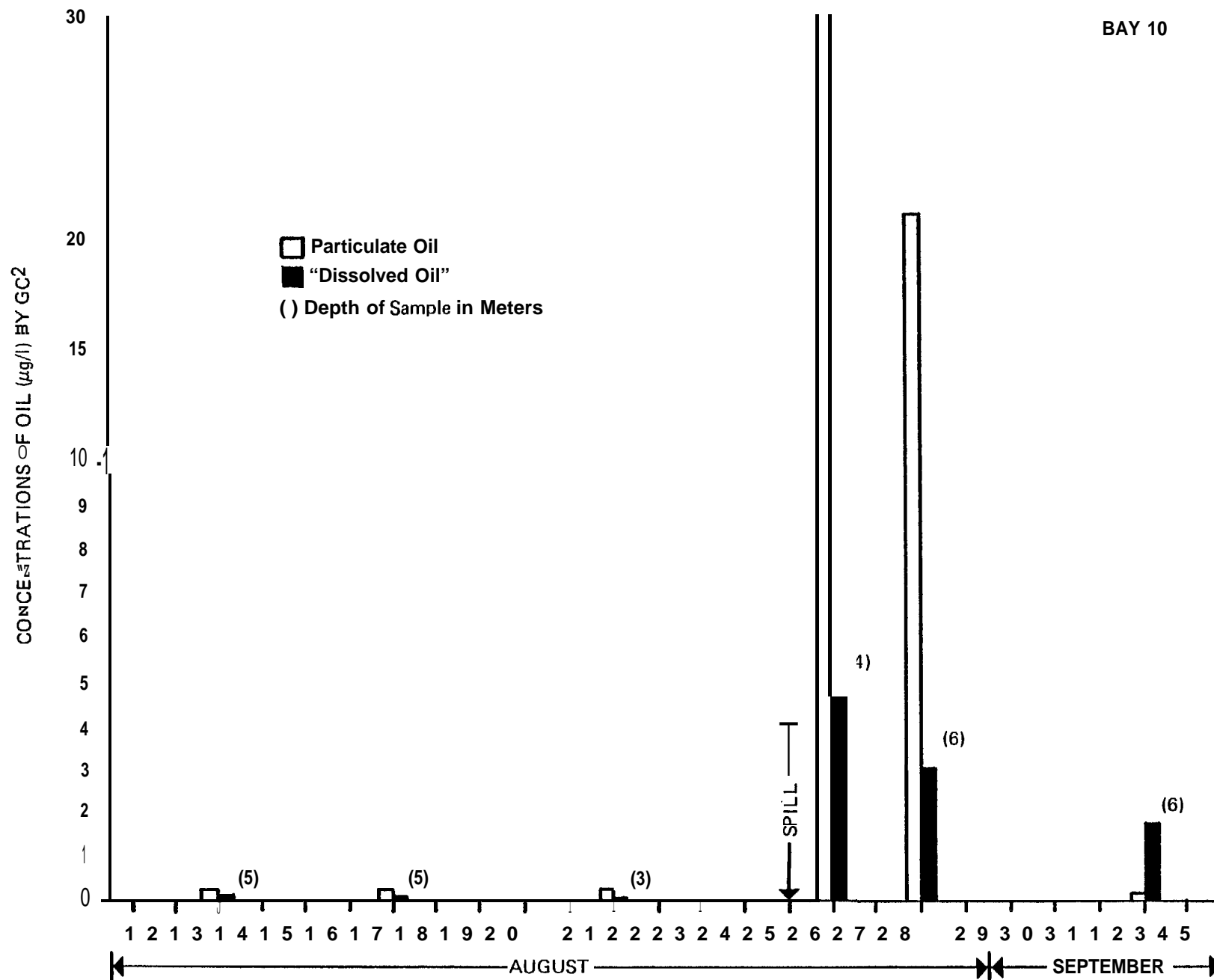
Figure 3.34. Large Volume Water Sample Concentrations (Bay 10).
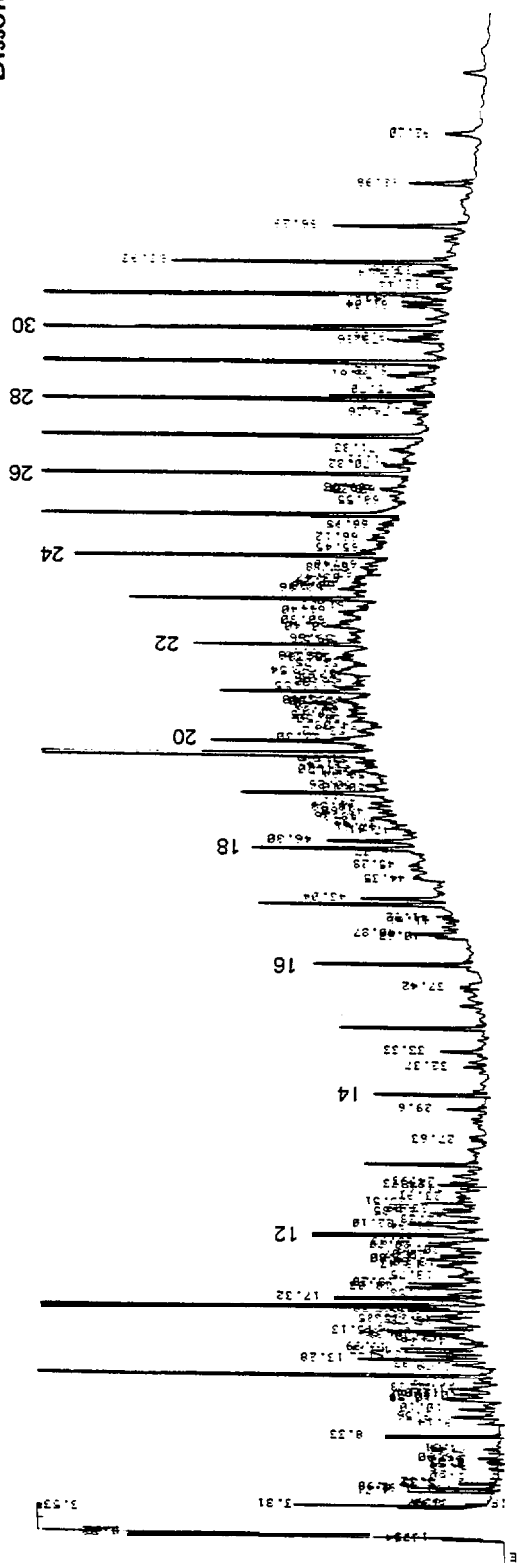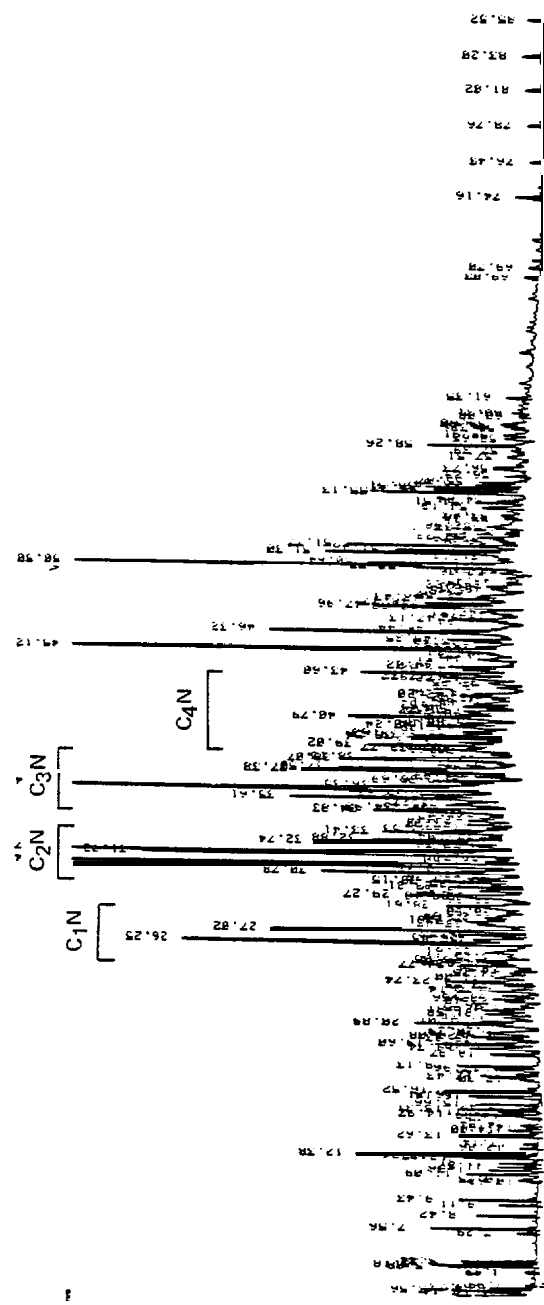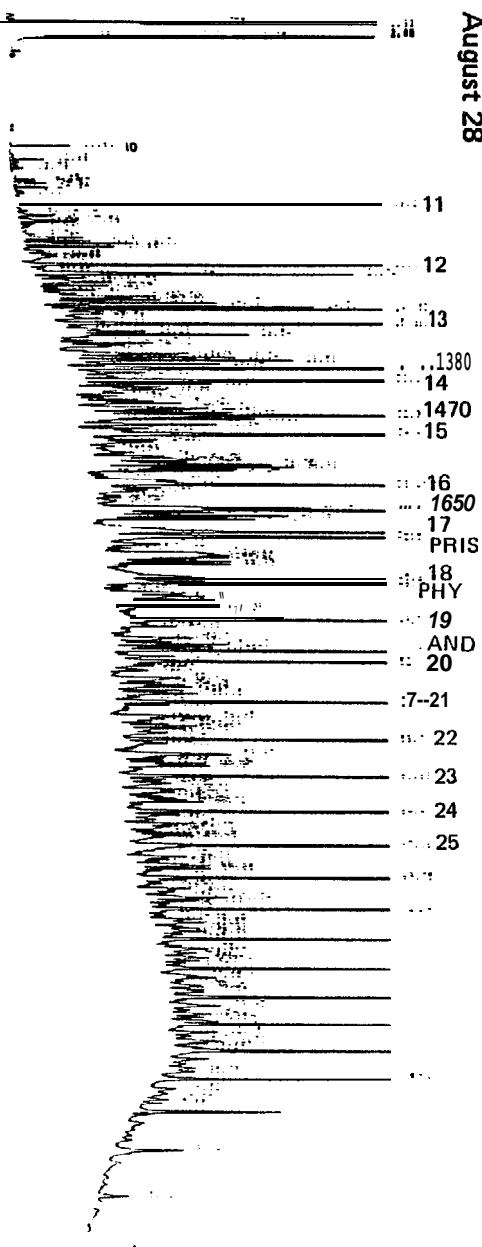
Figure 3.35. Large Volume Water Sample (Bay 0: August 28, 4 Meters)(GC2 Composition)
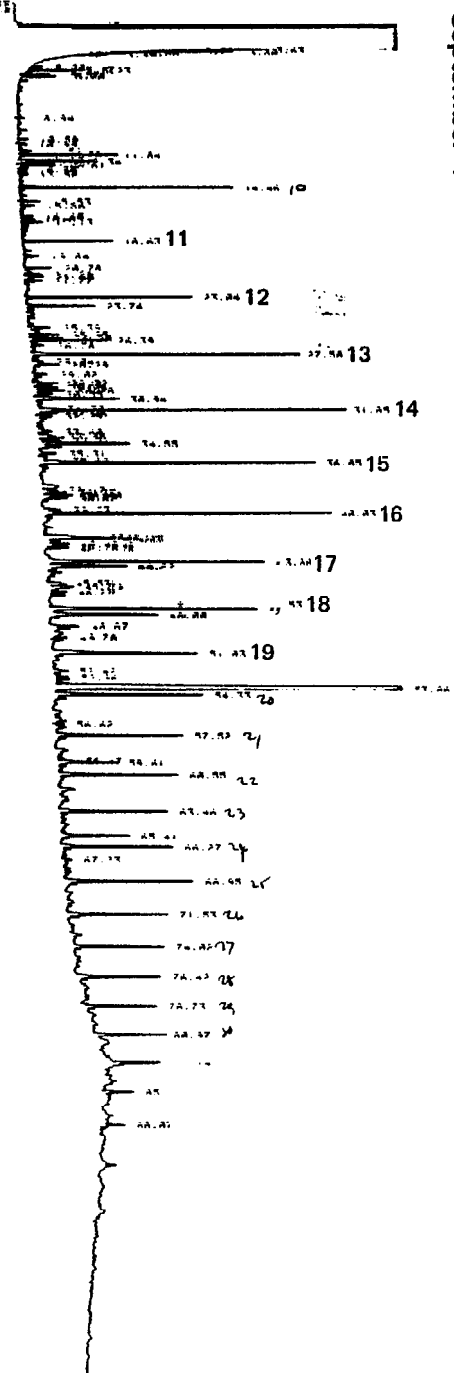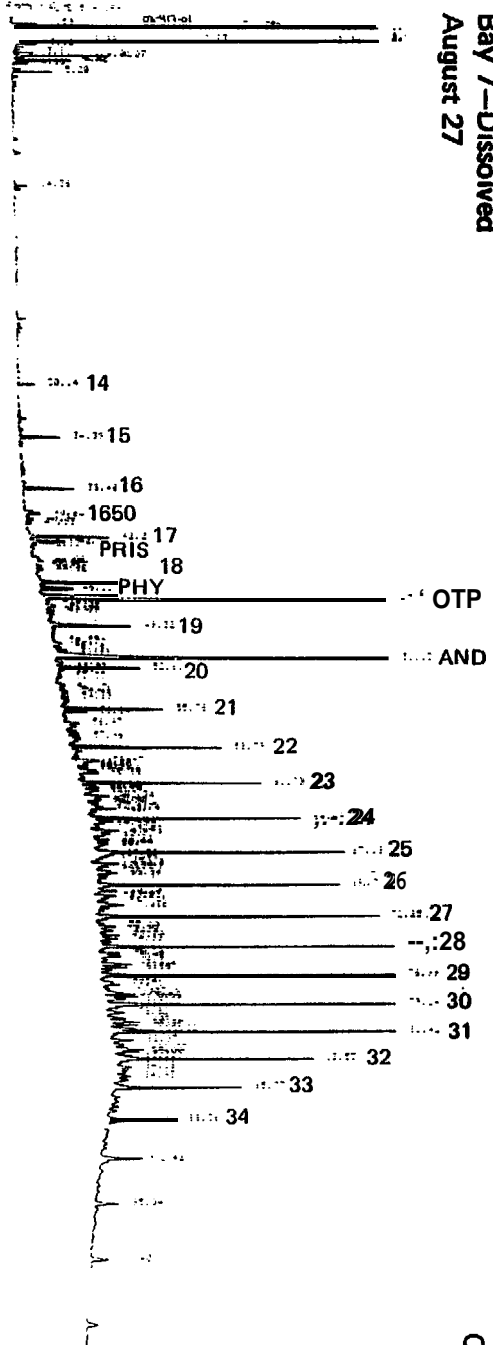
Figure 3.36. GC2 Profiles of Various Large Volume Water Samples.

3.1.2.3c Bay 7

Only three samples were obtained from Bay 7 (Table 3-7,
Figure 3-37). Low levels (2.6 ppb) of petroleum were
observed on the day of the Bay 9 (dispersed oil) spill,
mainly in the particulate form. In contrast, the waterborne oil
sampled from Bay 7 on August 29 was primarily in the filterable
(i.e., water-soluble/submicron tar) form (Figure 3-37). All
samples from Bay 7 consisted of a highly weathered saturate
hydrocarbon assemblage (Figure 3-36C). A representative
particulate/dissolved saturated hydrocarbon pair is illus-
trated in Figure 3-38). Levels returned to pre-spill values
between August 29 and September 6 (Table 3-7).

3.1.2.3d Bay 11

Water column monitoring using large volume samplers began
at Bay 11 prior to the surface oil (Bay 11) spill on August
19, and continued through August 25. An additional sample was
obtained on September 3. No samples were obtained during the
time period immediately following the dispersed oil (Bay 9)
spill on August 27 (see Figure 3-37; Table 3-7). Levels of oil
observed at 3 meters depth on August 19 were ∿6 µg/L. Surface
(1 m) samples obtained on August 20 were 10 µg/L. Detectable
levels of progressively more weathered particulate oil were
observed through September 3 (Table 3-7; Figure 3-39).

The total filterable or dissolved oil concentrations
are always at least a factor of two lower than the particulate
fraction, although a greater proportion of these compounds
are aromatic hydrocarbons. Compositionally the petroleum
hydrocarbons in Bay 11 which pass the filter most often are
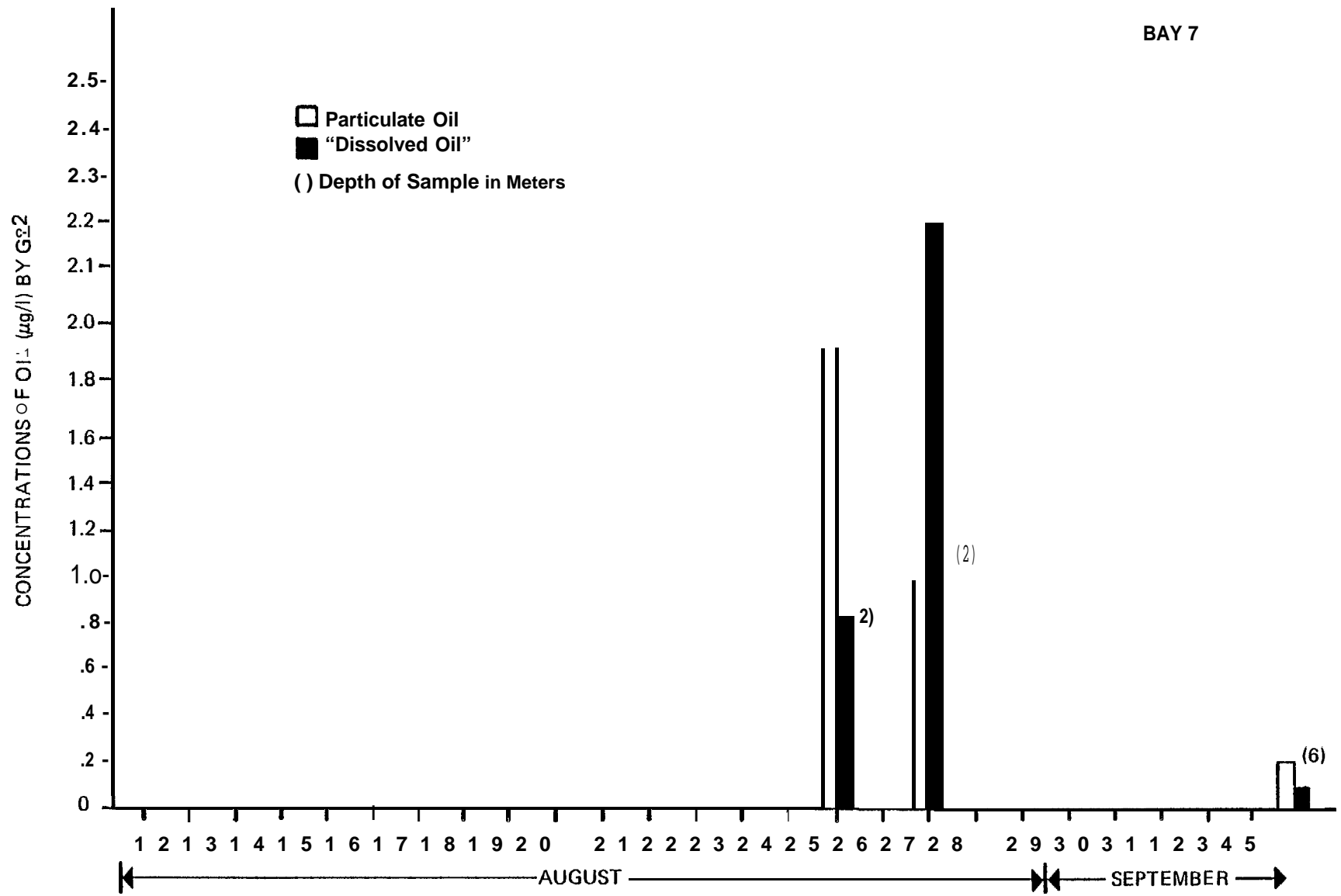comprised of low levels of high molecular weight n-alkanes

Figure 3.37. Large Volume Water Samples Concentrations (Bay 7).

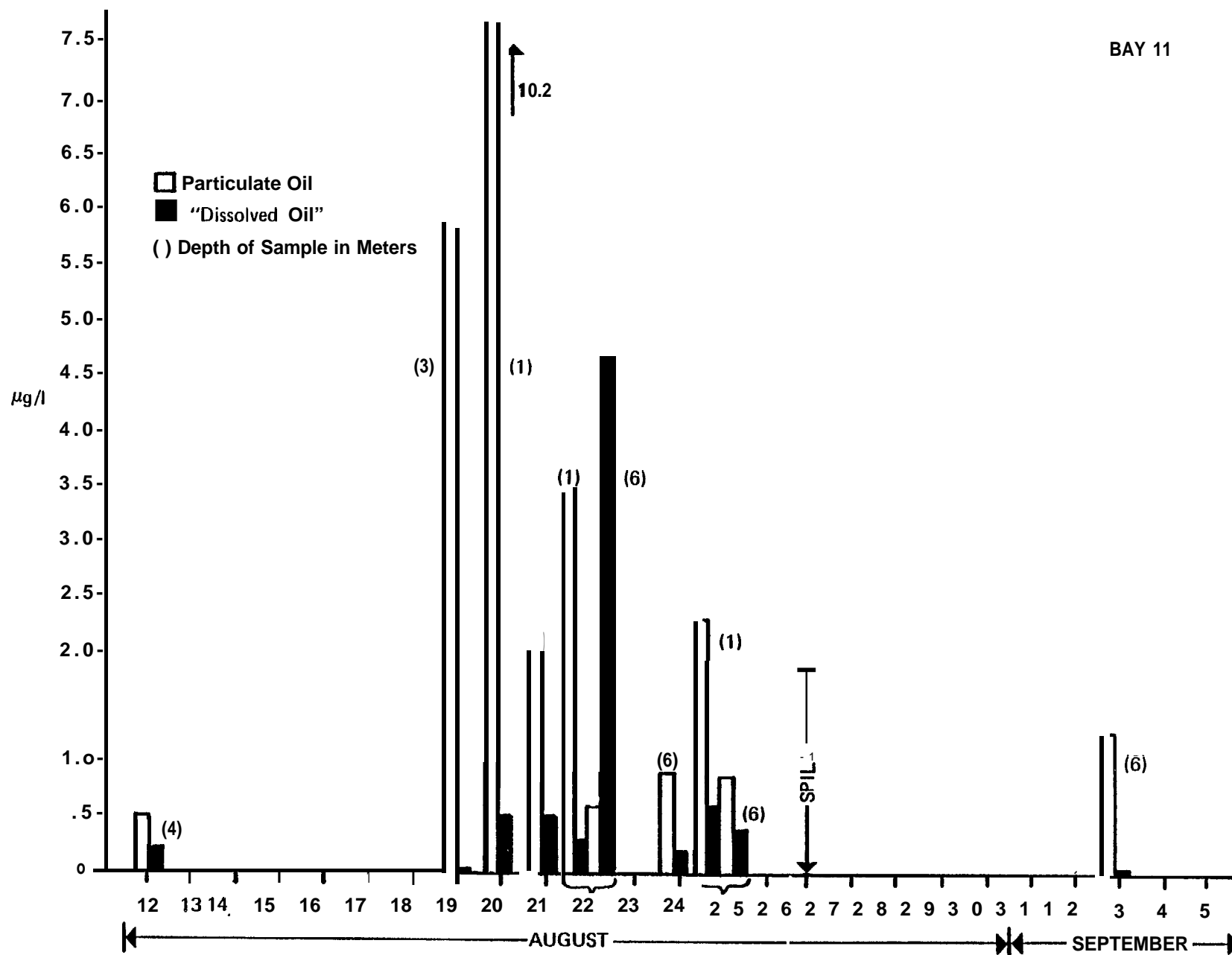**Figure 3.38. Large Volume HMWHC (Saturates)–Bay 7 (8/29)(GC^2 Compositions).**

Figure 3.39. Large Volume Water Sample Concentrations (Bay n).

with a significant unresolved complex mixture (UCM), and two-ringed aromatics (mainly naphthalenes) in the water-soluble fraction. The presence of this composite leads us to conclude that the filterable or dissolved material is actually a mix of submicron tar particles and truly dissolved aromatics. Some examples of the GC^2-derived compositions are indicated in Figures 3-40 and 3-41.

The petroleum in the water column in Bay 11 was detected in surface (1 m), midwater (3 m), and bottom (6 m) waters prior to the Bay 9 spill (dispersed oil). One may conclude that low levels of oil which eroded from the Bay 11 beach were transported to the benthos, a phenomenon confirmed by biotal data (see section 3.4).

3.2 Oil in the Sediments

Sediment samples were obtained from three sampling "grids" from the four bays prior to and during two samplings after the spillages of oil. Additionally, sediment floe (i.e., the diver acquired top 2-5mm of newly deposited sediment) was collected where present. All samples were analyzed by UV/F to determine gross petroleum (i.e., petroleum fluorescence equivalents) levels. However, the detection of low levels of petroleum equivalents by UV/F, as in pre-spill and other samples, did not necessarily indicate the presence of "oil" since background natural fluorescence does occur and is measured as "petroleum equivalents." Therefore GC^2 and GC^2/MS analyses were used to examine the compositional nature of oil in the sediments, and where very low (near background) levels of "petroleum equivalents" were measured, to ascertain whether oil was actually present.
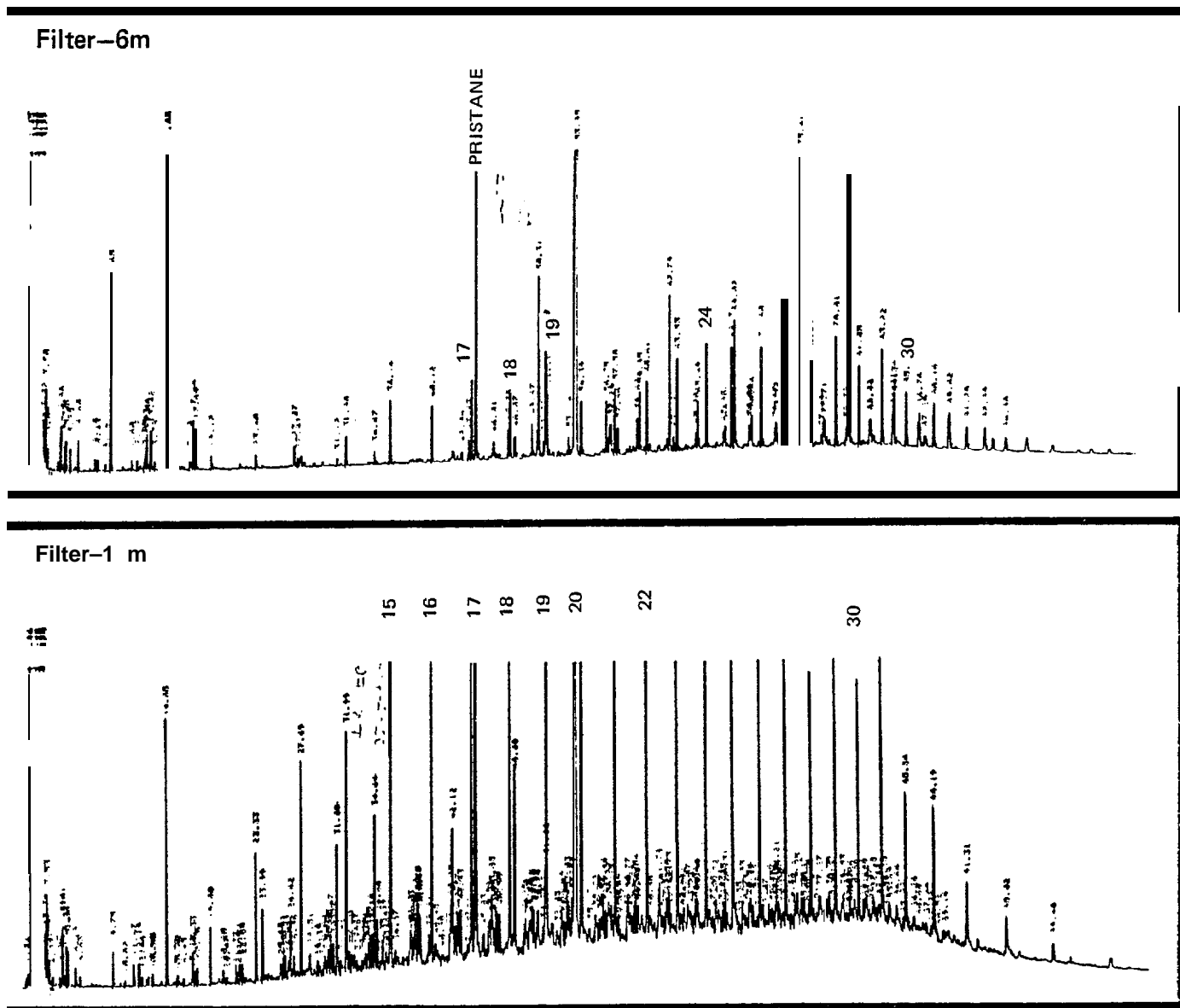
Filter—6m

PRISTANE

17 18 19' 24 30

Filter—1 m

15 16 17 18 19 20 22 30

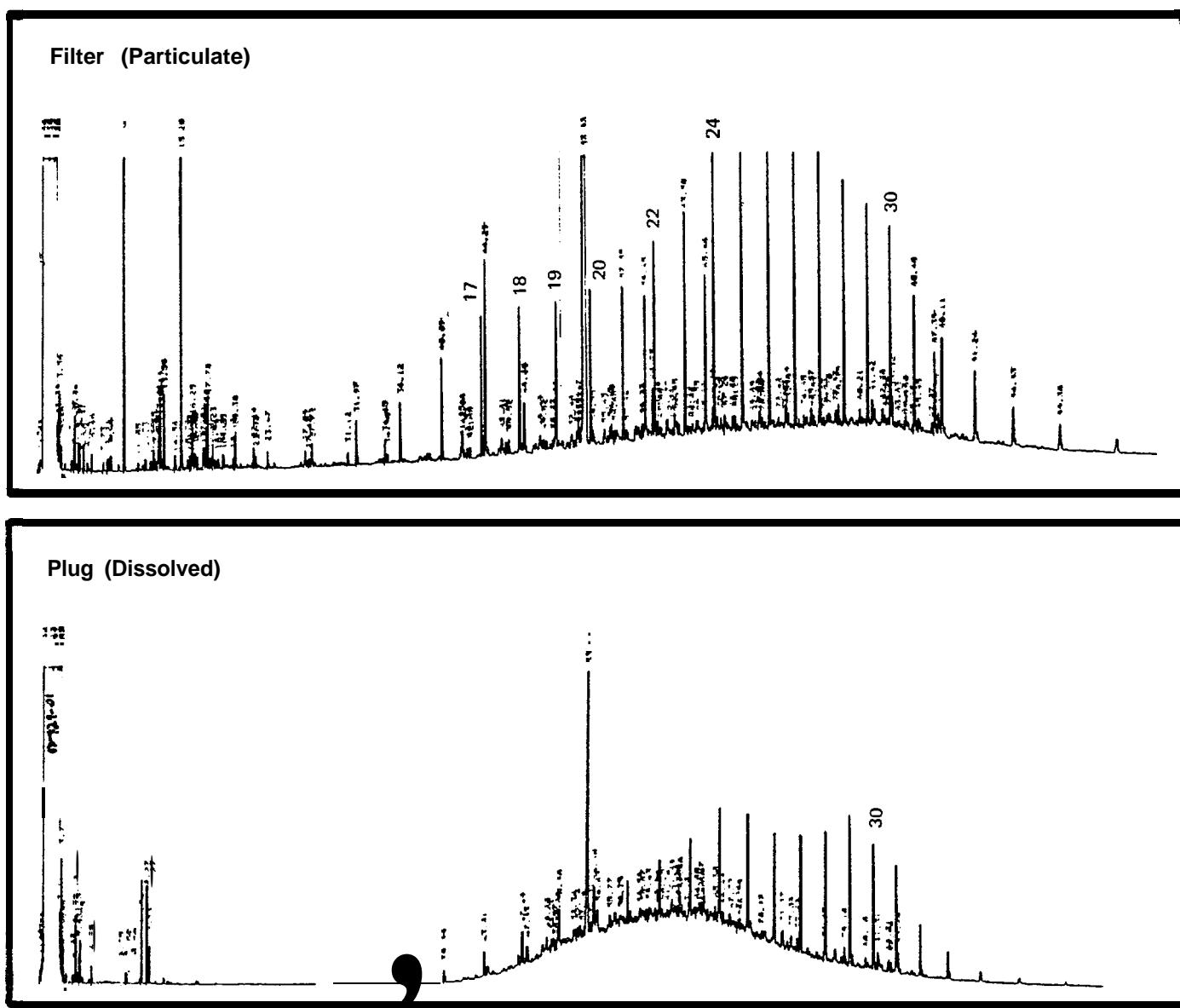Figure 3.40. Large Volume HMWHC (Saturates)–Bay 11 (8/25) (GC2 Compositions).

Figure 3.41. Large Volume HMWHC (Saturates)–Bay 11 (9/3)(GC^2 Compositions).

3.2.1 Bay 9

3.2.1.1 Tissue Plots (Sediments)

3.2.1.1a Tissue Plots (UV Sediments) Bay 9

Samples of surface sediment from the top two centimeters
of bottom material were collected from the tissue plots
(#1-10) of Bay 9 on August 10 (pre-spill), August 28
(+1day from the dispersed oil spill) and September 10
(+14 days from the dispersed oil spill). The divers scooped
the sediment surface with a glass jar and probably collected
some surface floe along with the surface sediment. Concentra-
tions of oil as determined by UV/F were reported in micrograms
per gram of dry sediment.

The levels of petroleum fluorescent equivalents in
sediments collected during the pre-spill sampling were
measurable (Figure 3.42) but less than 0.6 µg/g. The concen-
tration of petroleum equivalents was 0.38 (-. 13, 1.2)[1] and
0.34 (.13, .57)[1] µg/g for the 7 m and 3 m depth strata, respec-
tively. As discussed below, no petroleum was found in these
pre-spill samples, and the observed fluorescence was due to
naturally occurring fluorescent compounds. In general, con-
centrations less than 0.6 µg/g can be considered uncontaminated.

One day after the dispersed oil spill, the concentrations
of oil increased by an order of magnitude (7m: 2.1 [1.5, 2.7],
3m: 3.1 [1.9, 4.7] µg/g) (Figure 3.43). Concentrations of

---

[1]The UV fluorescence data is reported for each depth
stratum using the following convention: geometric mean (lower
95% confidence limit, upper 95% confidence limit). The
statistical calculations are discussed in Section 3.2.7, and a
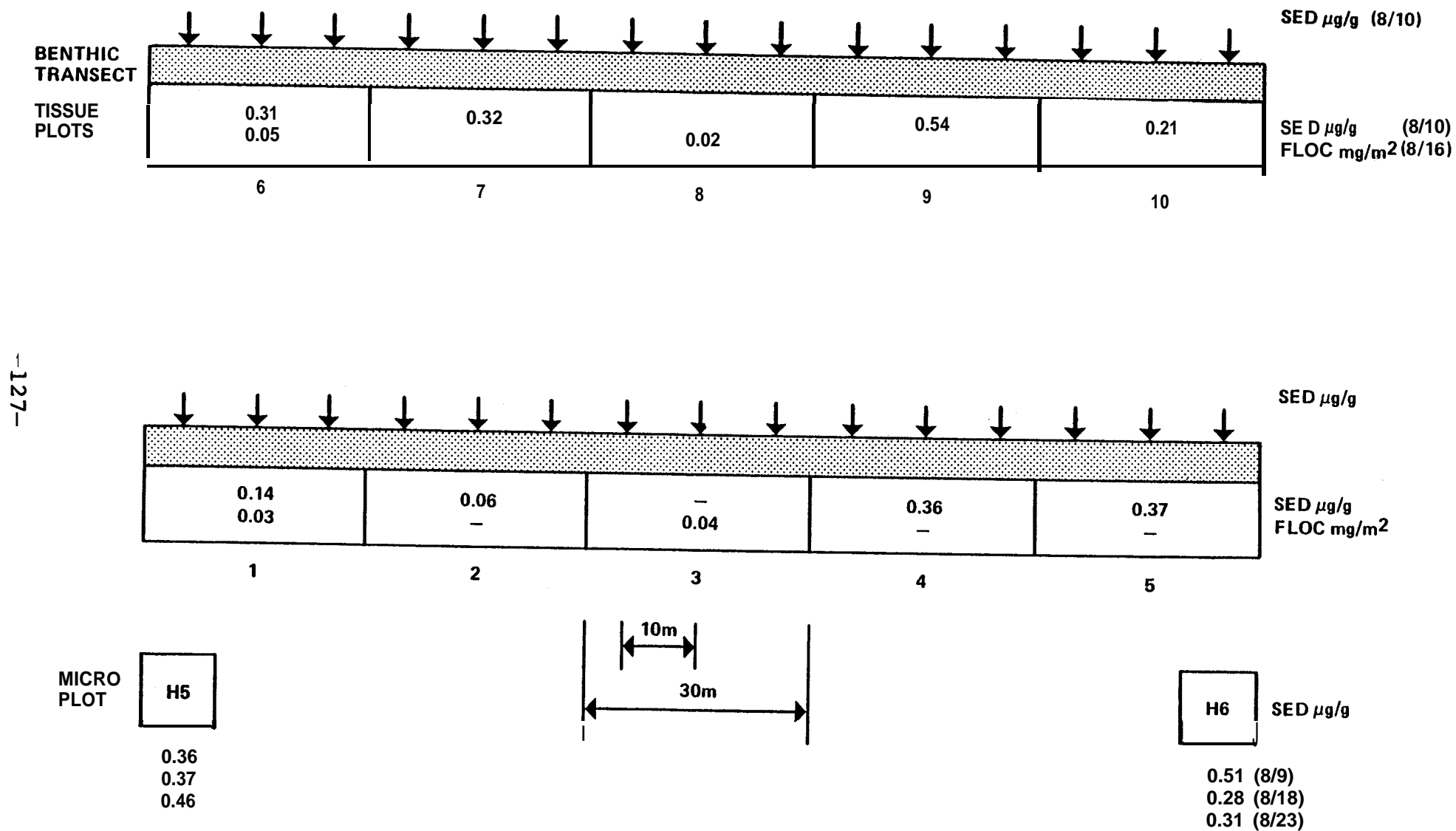summary of all calculations appears in Appendix A.

Figure 3.42. Oil Concentrations in Sediments and Floe by UV/F, Bay 9—Prespill.
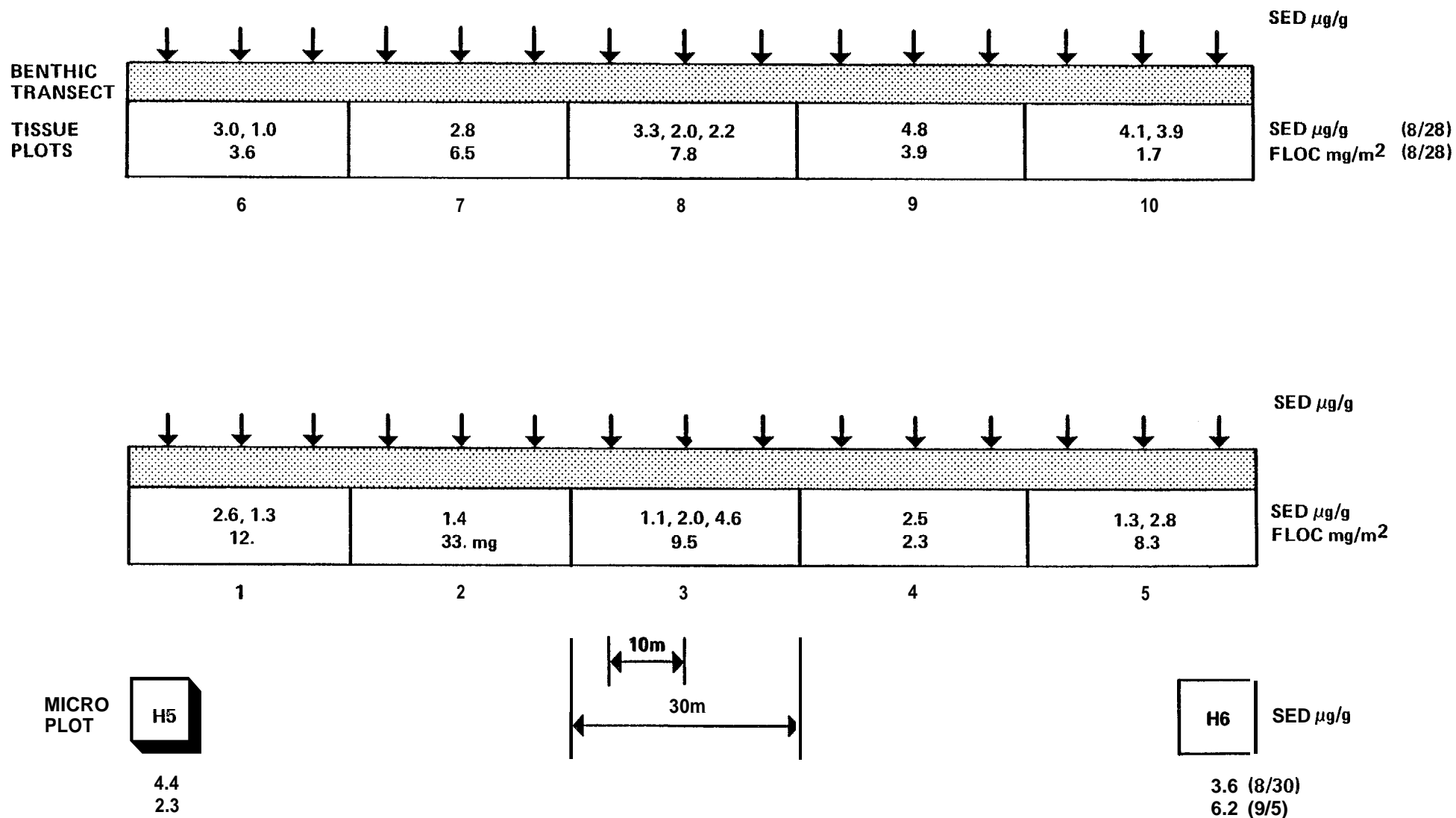
SED μg/g

BENTHIC
TRANSECT

3.0, 1.0	2.8	3.3, 2.0, 2.2	4.8	4.1, 3.9
3.6	6.5	7.8	3.9	1.7

TISSUE
PLOTS

SED μg/g (8/28)
FLOC mg/m² (8/28)

6   7   8   9   10

SED μg/g

2.6, 1.3	1.4	1.1, 2.0, 4.6	2.5	1.3, 2.8
12.	33. mg	9.5	2.3	8.3

SED μg/g
FLOC mg/m²

1   2   3   4   5

10m

30m

MICRO
PLOT   H5

H6   SED μg/g

4.4
2.3

3.6 (8/30)
6.2 (9/5)

Figure 3.43, Oil Concentrations in Sediments and Floe by UV/F, Bay 9–Ist Postspill.

oil continued to increase significantly (7m: 9.0 [5.2, 15],
3m: 5.3 [2.4, 11] µg/g) by two weeks after the dispersed oil
spill (Figure 3.44).   The observed increase in petroleum
concentrations over the two week time period following the
spill may have been due to a lag in the sedimentation and
incorporation of oil into the sediment, or transport of more
highly oiled sediments from outside of the study area.   The
variability of petroleum concentrations within the study area
was low for both post-spill samplings, which suggests a
relatively homogeneous oiling of Bay 9 sediments.   The two
depth strata were statistically indistinguishable from each
other for all three samplings.

3.2.1.1b Oil Composition by GC^2

GC^2 analyses were performed on samples from four
stations from each of the post-spill sampling periods.
Due to low background levels of hydrocarbons it is relatively
straightforward to identify oil-impacted sediments from
their f_1 (saturates) GC^2 trace oil.   Several generalities
can be stated:

    a.   There is no evidence for biodegradation of oil in
       any of the sediments.   The GC^2 profiles and the
       relative abundance of **n-alkanes** and isoprenoids
       remains constant in oiled sediments from all bays
       and at **all** times.

    b.   The **pre-spill** and unoiled sediments contain prominent
       $n-C_{17}$, **pristane**, n-25, $n-C_{27}$, $n-C_{29}$, $n-C_{31}$, $n-C_{33}$
       peaks indicating a mix of marine and terrigenous
       biogenic molecules.

    c.   A very high pristane (**biogenic**) to phytane (**petrogenic**)
       ratio in **pre-spill** samples >10 gives way to a lower
       value (<3.5) due to inputs of petrogenic **phytane.**
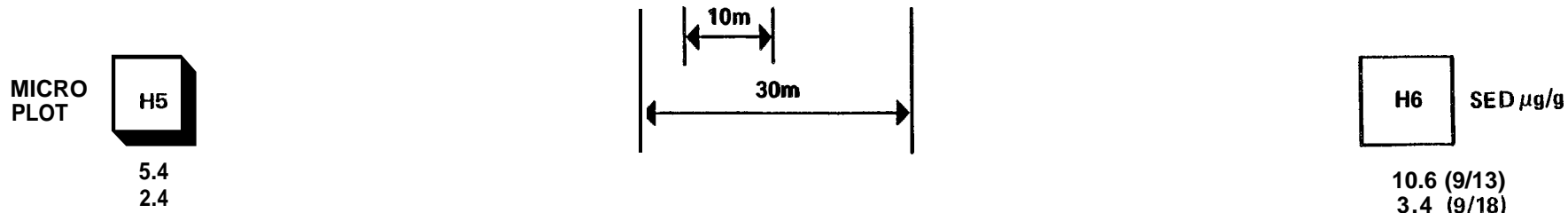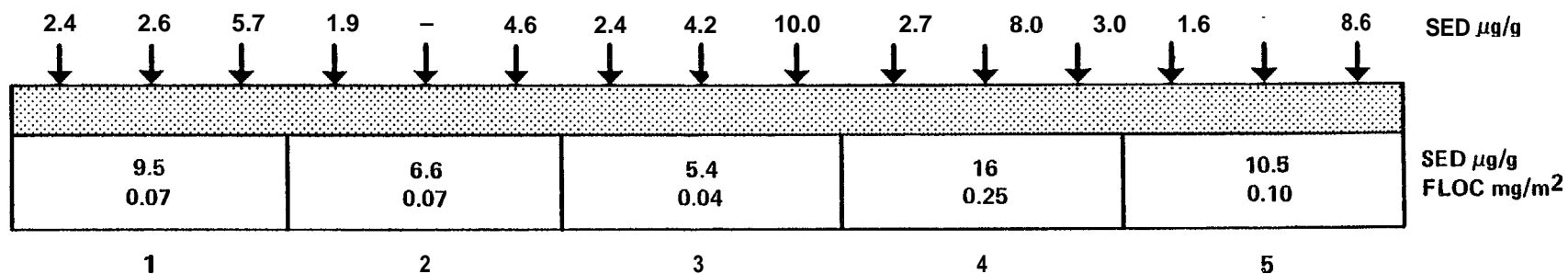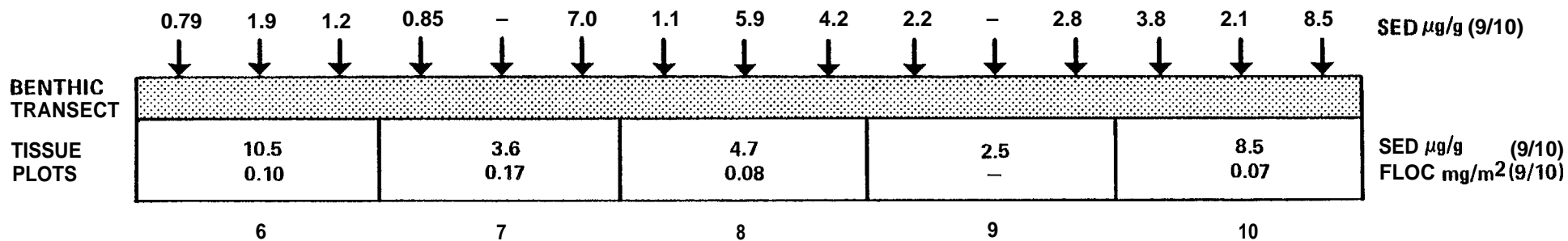   The more oil, the lower the ratio as it approaches
       that for oil (∼0.6).

BENTHIC TRANSECT

| 0.79 | 1.9 | 1.2 | 0.85 | – | 7.0 | 1.1 | 5.9 | 4.2 | 2.2 | – | 2.8 | 3.8 | 2.1 | 8.5 |

SED µg/g (9/10)

TISSUE PLOTS

| 10.5 0.10 | 3.6 0.17 | 4.7 0.08 | 2.5 – | 8.5 0.07 |

SED µg/g (9/10)
FLOC mg/m^2 (9/10)

| 6 | 7 | 8 | 9 | 10 |

| 2.4 | 2.6 | 5.7 | 1.9 | – | 4.6 | 2.4 | 4.2 | 10.0 | 2.7 | 8.0 | 3.0 | 1.6 | | 8.6 |

SED µg/g

| 9.5 0.07 | 6.6 0.07 | 5.4 0.04 | 16 0.25 | 10.5 0.10 |

SED µg/g
FLOC mg/m^2

| 1 | 2 | 3 | 4 | 5 |

|← 10m →|

30m

MICRO PLOT   H5

5.4
2.4

H6   SED µg/g

10.6 (9/13)
3.4 (9/18)

Figure 3.44. Oil Concentrations in Sediments and Floe by UV/F, Bay 9–2nd Postspill.

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d. A high carbon preference index (CPI) = $2(n\text{-}C27 + n\text{-}C_{29})/(n\text{-}C_{26} + 2n\text{-}C_{28} + n\text{-}C_{30})$ in unoiled samples (5-10) gives way to a lower value (≤ 3.5) in oiled sediments due to inputs of even carbon number normal alkanes.

e. An odd/even preference ratio in the $n\text{-}C_{12}$ to $n\text{-}C_{20}$ region would clearly indicate the absence of oil. Even chain n-alkanes in this boiling range are present in very small quantities in pre-spill or unoiled sediments while oil is abundant in these compounds.

A representative set of GC^2 traces for oiled and unoiled sediments (Figure 3-45) illustrates these points as does an n-alkane plot (Figure 3-46). In this latter graph (Figure 3-46) unoiled sediments are seen to be influenced by $n\text{-}C_{15}$, and $n\text{-}C_{17}$ (planktonic origin), as well as the odd-carbon higher molecular weight n-alkanes. Oiled sediments add considerable n-alkane material in the $n\text{-}C_{12}$ to $n\text{-}C_{28}$ range and cause an overall lowering of the odd/even alkane predominance.

A summary of the key GC^2-derived parameters to Bay 9 sediment is presented in Table 3-9. All Bay 9 sediments from both post-spill samplings contain oil as evidenced by low parameter ratios. Station 1 seems least impacted initially, although oil is clearly present, as the ratios are somewhat higher than those from the other stations. Virtually no qualitative change takes place between one day and two weeks after the spill.

3.2.1.1c Composition of Aromatic Hydrocarbons by GC^2/MS

The results from two samples of Bay 9 sediment from the two time intervals (Figure 3.47) illustrate another fact of oil spill chemistry. Low levels of naphthalene, phenanthrene
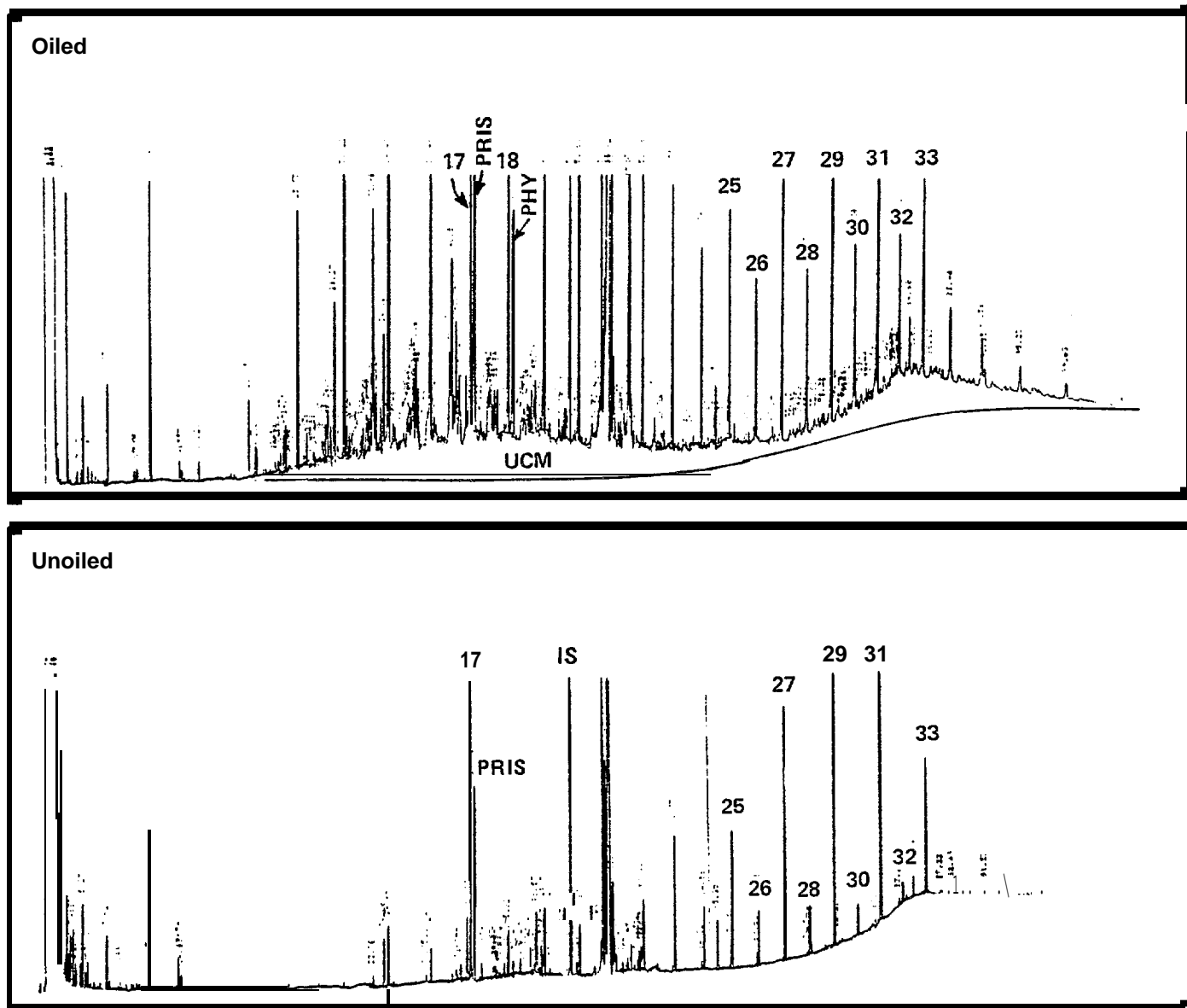
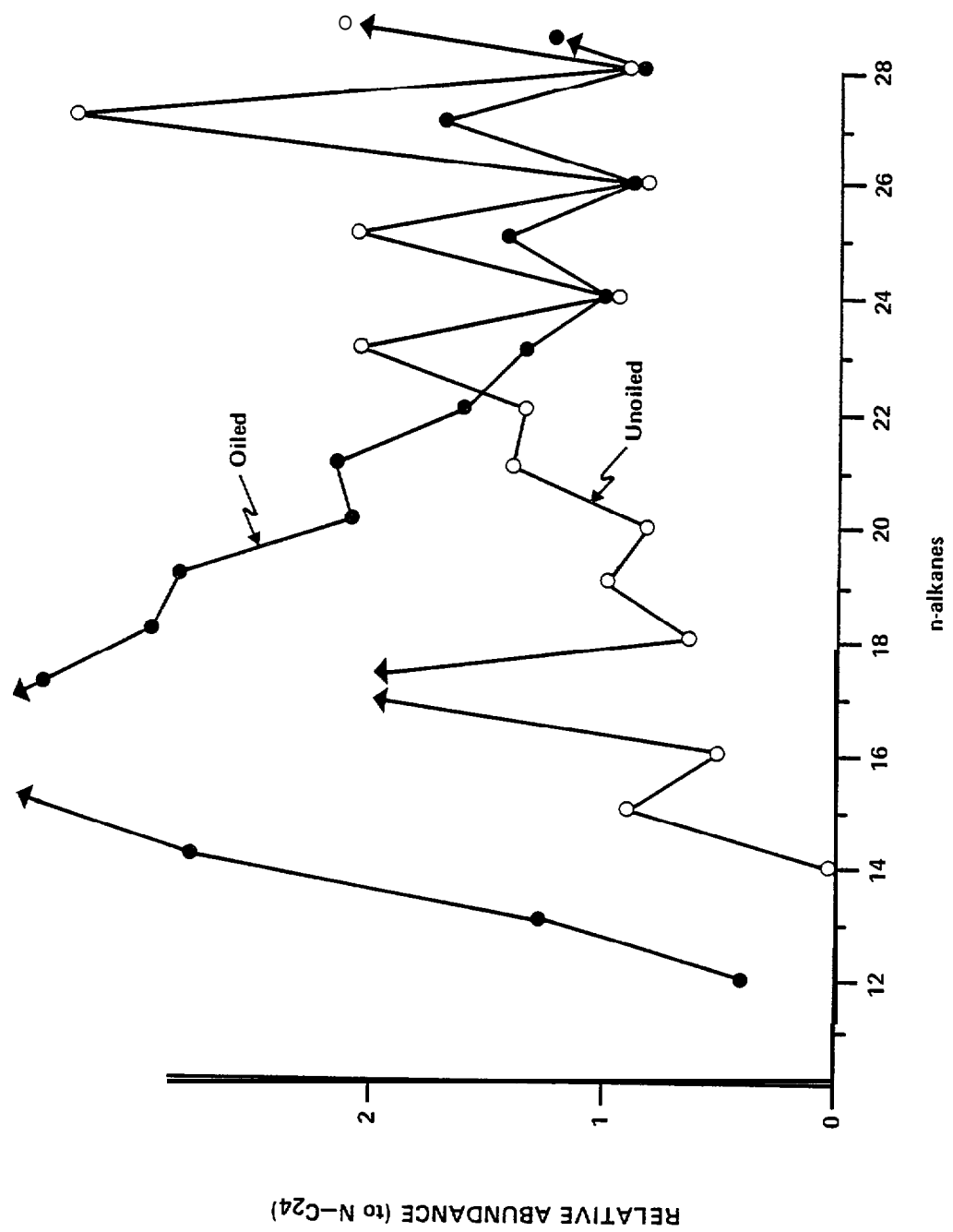**Figure 3.45. Typical Sediment GC Traces (Saturates).**

Figure 3.46. Typical n-alkane Profiles of Oiled & Unoiled Sediments.

TABLE 3-9

SEDIMENT HYDROCARBON SOURCE SUMMARY:
GC^2 RESULTS TISSUE PLOTS

SAMPLE	PRIS/PHY	CPI	STATUS
BAY 9			
First Post-Spill			
Station 1	3.6	3.5	Oil
5	1.9	2.2	Oil
6	2.5	2.7	Oil
10	2.0	2.6	Oil
Second Post-Spill			
Station 1	1.2	1.9	Oil
5	1.3	**2.3**	Oil
6	1.2	1.9	Oil
10	2.1	2.3	Oil
BAY 10			
First Post-Spill			
Station 1	3.5	4.1	Oil
3	4.6	7.9	No Oil
5	1.9	3.6	Oil
6	2.6	5.0	Oil
10	3.5	2.8	Oil
Second Post-Spill			
Station 6	3.0	3.0	Oil
10	2.4	3.1	Oi 1
BAY 7			
First Post-Spill			
Station 1	21	8.6	No Oil
3	8	6.2	No Oil
5	18	11.0	No Oil
Second Post-Spill			
Station 1	7.3	8.9	No Oil
4	5.4	5.4	No Oil
5	9.3	8.7	No Oil
10	3.0	3.0	Oil
BAY 11			
Second Post-Spill			
Station 1	1.8	2.3	**Oil**
5	2.0	3.4	**Oil**
6	3.6/3.6[a]	5.2/3.3[a]	Oil (Low)
10	**6.6/6.4**[a]	3.1/3.0[a]	Oil (Low)
OIL	0.75	1.0	
Baseline	>10	>5	

[a]Duplicate analyses

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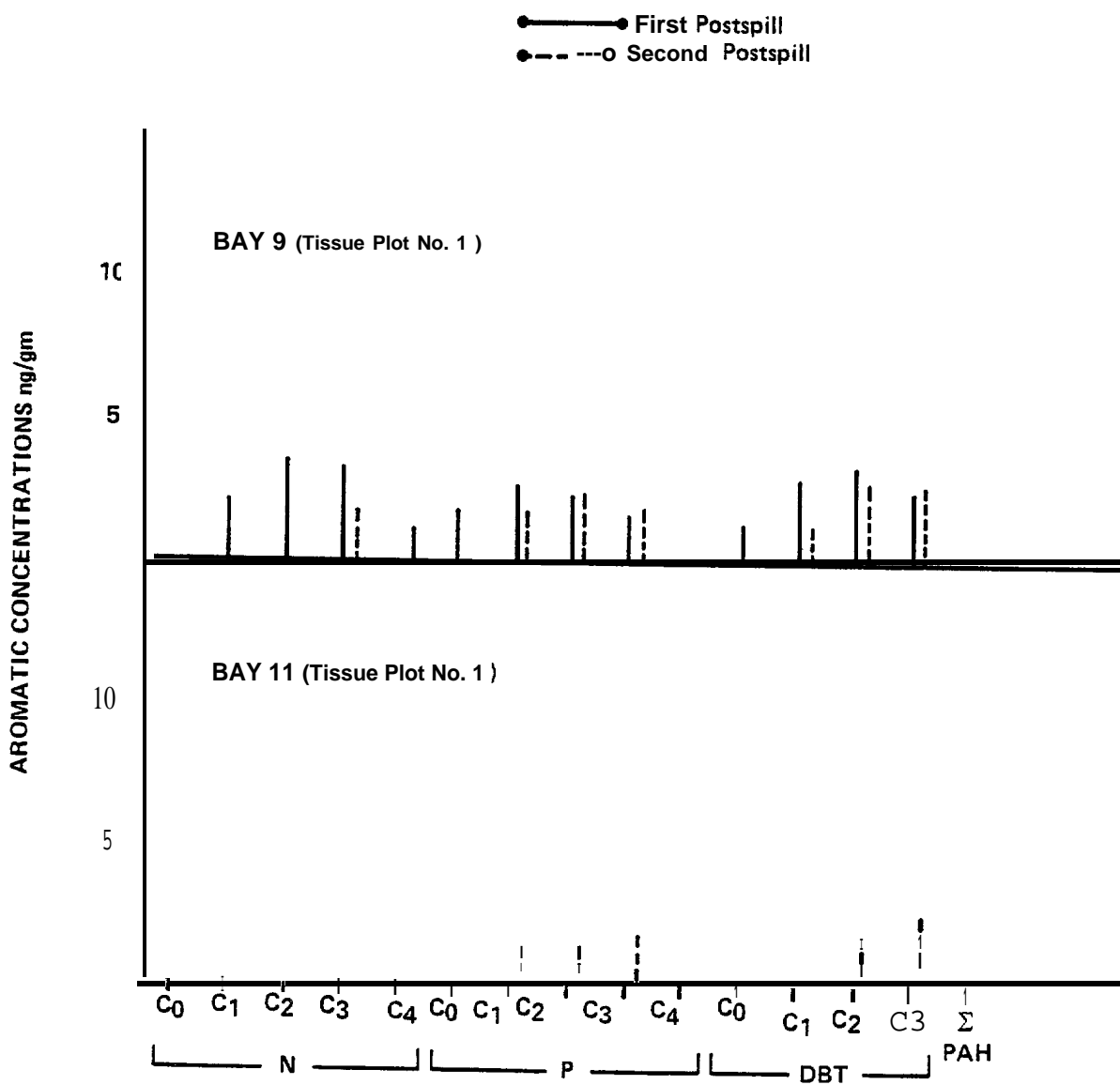
Figure 3.47.. **Bays** 9 **and 11 Sediments (Aromatic Hydrocarbons) by** GC2/MS.

and **dibenzothiophene** compounds remain nearly constant over two weeks, but the more soluble aromatics (C_1, C_2 naphthalenes, phenanthrene) are lost from the samples.

3.2.1.2 Tissue Plots (Floe) - Bay 9

3.2.1.2a Oil Concentrations by UV\F

Samples of floe, unconsolidated fine particulate and detritus at the sediment/water interface, were collected from the tissue plots of Bay 9 on August 16 (prespill), August 28 (+1 day from the dispersed oil spill) and September 10, 1981 (+14 days from the dispersed oil spill). Concentrations of petroleum are reported in milligrams per sediment surface area (mg/m^2). The four prespill samples which were analyzed contain negligible concentrations (<.05 mg/m^2) of petroleum (Figure 3.42). Levels of petroleum in floe collected during the first post spill sampling (Figure 3.43) were elevated and ranged from 2 to 33 mg/m^2 (7m: 9.70 [2.8, 29], 3m: 4.3 [2.0, 8. 3] mg/m^2. By the second post spill sampling (Figure 3.44), the levels had dropped almost to background concentrations (7m: 0.10 [.01, .21], 3m: 0.10 [.04, . 18] mg/m^2). Statistically, the first post spill sampling differs from the prespill and second post spill sampling which do not differ from each other (Table 3.10).

Typical UV/F spectra from Bay 9 floe samples (Figure 3.48), illustrate the appearance of a peak at 355 nm in the first post spill sampling. This peak results from the incorporation into the floe of three- and four-ringed aromatic hydrocarbons present in the oil. The two-ring peak at 310 nm is obscured by a signal in the procedural blanks and in naturally occuring fluorescent compounds. The

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TABLE 3-10

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY
UV/F IN SEDIMENT AND FLOC OF BAY 9

SAMPLING	STATION	FLOC (mg/m^2)	SEDIMENT $(\mu g/g)$	$\dfrac{FLOC}{SEDIMENT}$[1]
Prespill	1	.03	.14	<1%
	2	---	.06	
	3	.04	---	
	4	---	.36	
	5	---	.37	
	6	.05	.31	<1%
	7	---	.32	
	8	.02	---	
	9	---	.54	
	10	---	.21	
1st post spill	1	12	2.0	30%
	2	33	1.4	120%
	3	9.5	2.6	14%
	4	2.3	2.5	5%
	5	8.3	2.0	21%
	6	3.6	2.0	9%
	7	6.5	2.8	12%
	8	7.8	2.5	16%
	9	3.9	4.8	4%
	10	1.7	**4.0**	2%
			Average	23%
2nd post spill	1	.07	9.5	<1%
	2	.07	6.6	<1%
	3	.04	5.4	<1%
	4	.25	16	<1%
	5	.10	10.5	<1%
	6	.10	10.5	<1%
	7	.17	3.6	<1%
	8	.08	4.7	<1%
	9		2.5	
	10	.07	8.5	<1%
			Average	<1%

[1]The floc/sediment ratio **assumes a conversion equation
of floc** (mg/m^2) **0.05 =** sediment $(\mu g/g)$. See text for the
derivation of the factor.
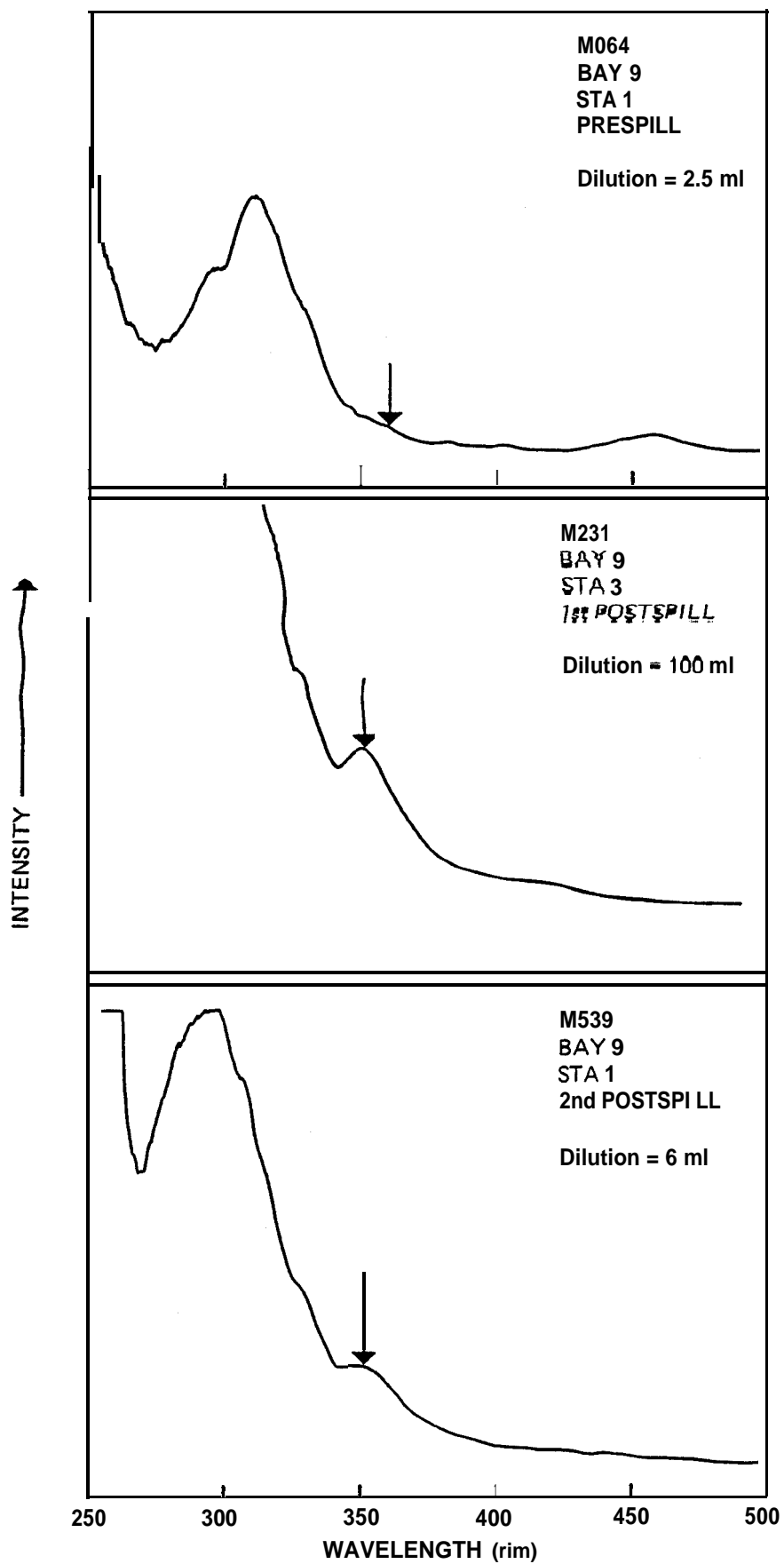
Figure 3.48. UV Spectra of Floc from Bay 9 (Note Dilution Factors).

persistence of the 355 nm peak in the second post spill
spectra suggests that low levels of petroleum may be still
present in the floe although absolute levels are not statis-
tically different from pre-spill values.

By making a few assumptions, the concentrations of oil
in floe can be compared to concentrations of bulk sediment.
Assuming a bulk sediment density of 2 g/cm^3, a water con-
tent of 50% and a sampling depth of 2 cm, one microgram of
oil/gram dry weight of sediment is equivalent to 20 mg/m^2
(Table 3-11). Using this conversion factor, the floe
comprises a negligible portion (<1%) of the oil in the
bottom sediment during the pre-spill and second post-spill
sampling and a significant fraction ($\sim$20%) during the first
post-spill sampling (Table 3-10).

3.2.1.2b   Oil Composition by GC^2

A total of 6 floe samples from Bay 9 stations were
fractionated and analyzed by GC^2. All 6 floe samples
analyzed from the one-day post spill samplings contained
moderately to heavily weathered (SHWR = 1.2-1.6) but unbio-
degraded (ALK/ISO $\cong$ 2.5) oil, while only very low levels of
oil were detectable by GC^2 in the two-week samples as iden-
tified by the low levels of n-alkanes in the GC^2 traces of
the samples. Two representative GC^2 (f_1, f2 pairs) are
shown in Figures 3.49 and 3.50. The GC^2 traces of the
saturated hydrocarbon fractions indicate that sedimented
petroleum, undiluted by significant amounts of sediment,
as would be evidenced by odd chain terrigenous n-alkanes
($C_{25}-C_{31}$), are captured in the floe samplings. This indi-
cates that only a thin slice of deposited surface sediment
is being sampled (several millimeters).

TABLE 3-11

DERIVATION OF THE CONVERSION OF SEDIMENT AND FLOC DATA

Knowns

Sediment concentrations are reported as $\mu g/g$ dry weight
Floe concentrations are reported as mg/m^2 area

Assumptions

The density of wet sediment is $2\ g/cm^3$

The water content of the sediment is 50%

The sediment was sampled to a depth of 2 cm

Calculations

$$Area = \frac{Volume}{Depth} = \frac{Wt}{p} \times \frac{1}{Depth}$$

and 1 g of dried sediment has an area of $0.50\ cm^2$

$$Thus\ 1\ \mu g/g\ dry\ sediment = \frac{1\ \mu g}{.5\ cm^2} \times \frac{1\ mg}{10^3} \times \frac{10^4\ cm^2}{1\ m^2} = 20\ \frac{mg}{m^2}$$
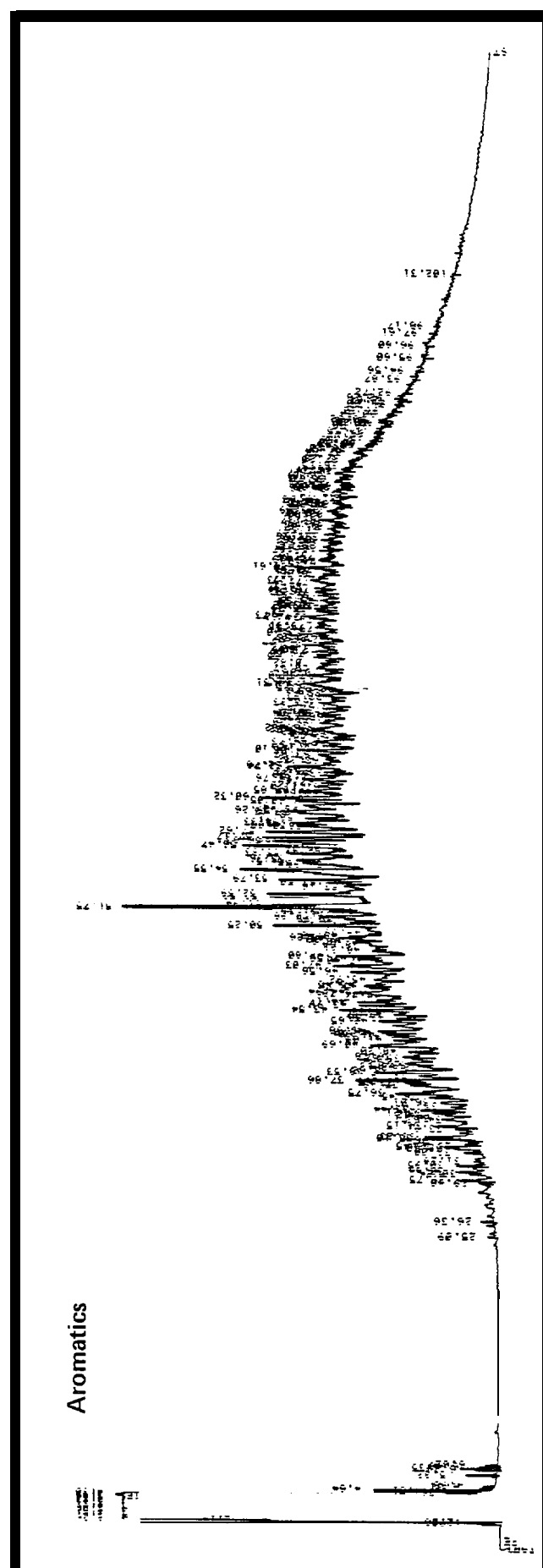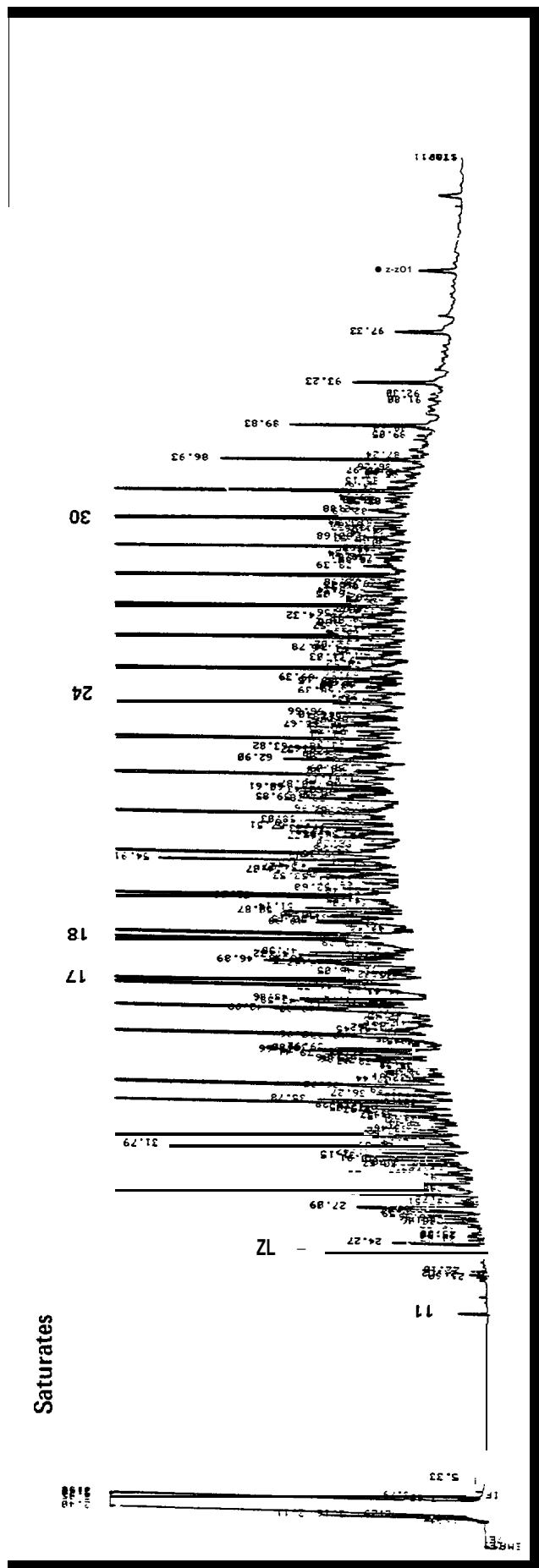
Figure 3.49. GC^2 Traces of Surface Floc from Bay 9—Station 2 (1st Postspill).

*Alkylated DBT and P Compounds

Figure 3.50. GC^2 Traces of Surface Floc from Bay 9–Station 5 1st Postspill).
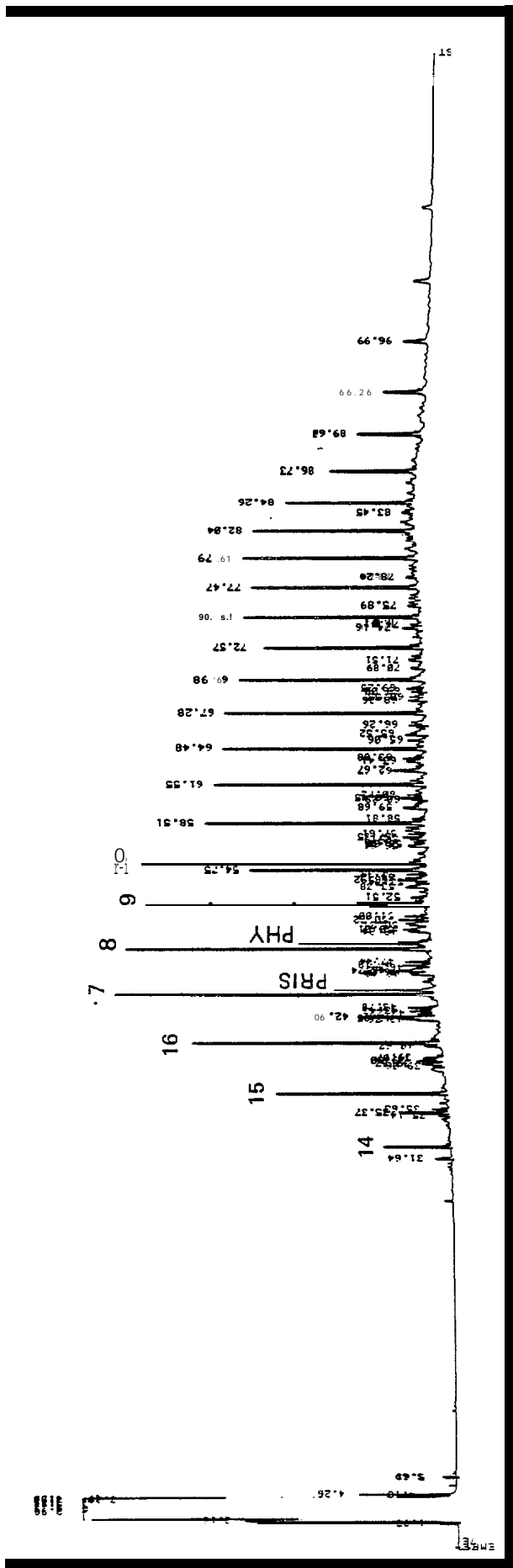
3.2.1.2c Aromatic Hydrocarbon Composition by GC^2/MS

GC^2/MS analyses were performed on three samples of
floe from Bay 9. The resulting aromatic hydrocarbon data
indicate that the heavily impacted floe (i.e., concentra-
tions greater than 10 mg/m^2) contains lightly to moderately
weathered aromatic residues. Floe aromatic composition
(Figure 3.51) consists of **alkylated** naphthalene, **phenan-**
threne and **dibenzothiophene** residues (500 µg/m^2 total) **in**
the one-day post-spill sampling. However, only negligible
amounts of **alkylated** phenanthrenes are detected at two
weeks, indicating, along **with** GC2 data, that oil-impacted
floe **is** a transient **entity in** these systems.

3.2.1.3 Biology Stations (Sediments) - Bay 9

3.2.1.3a Oil Concentrations by UV/F

Samples of surface sediment from the biology stations
of Bay 9 were collected August 28 (+1 day) and September 10
(+14 days). **Divers** scraped the top two centimeters of
sediment from stations located at 10 m increments along the
two depth strata. The sampling points were designated by
the distance from the northerly end of each transect which
was 150 m long. Both the collection and analysis of the
biology station samples were identical to those for the
tissue plot sediment samples. Only the samples collected
during the second post-spill sampling were analyzed.

The geometric mean concentrations of petroleum meas-
ured at stations located on the 3 meter and 7 meter depth
strata **in** Bay 9 were 2.7 (1.6, 4.2) and 3.8 (2.6, 5.5) µg/g,
respectively (Figure 3-44). The mean concentrations are
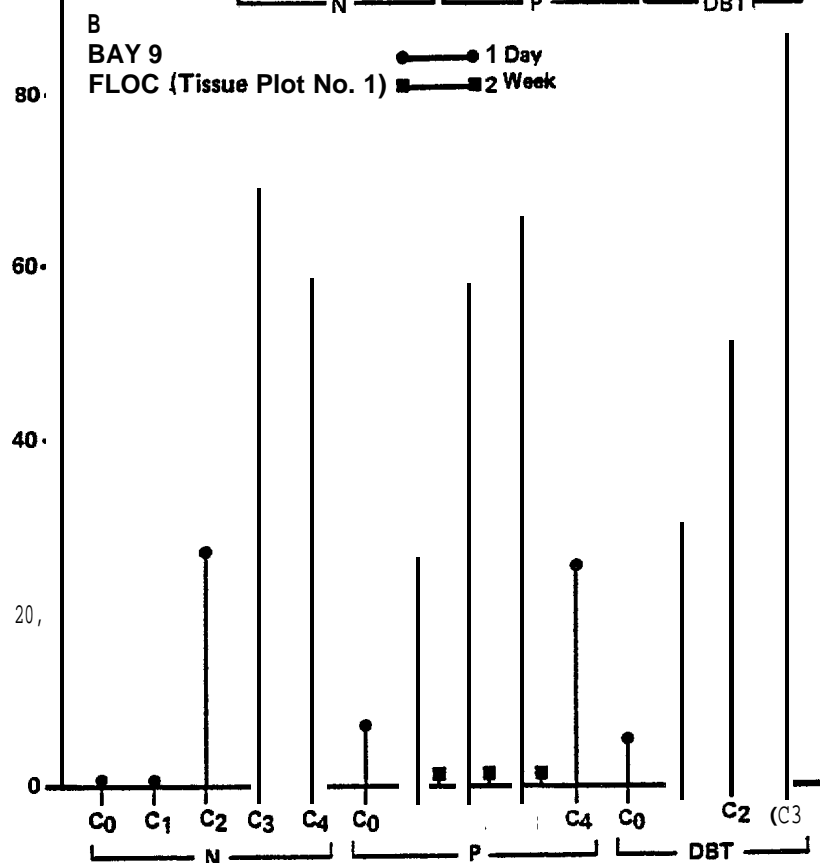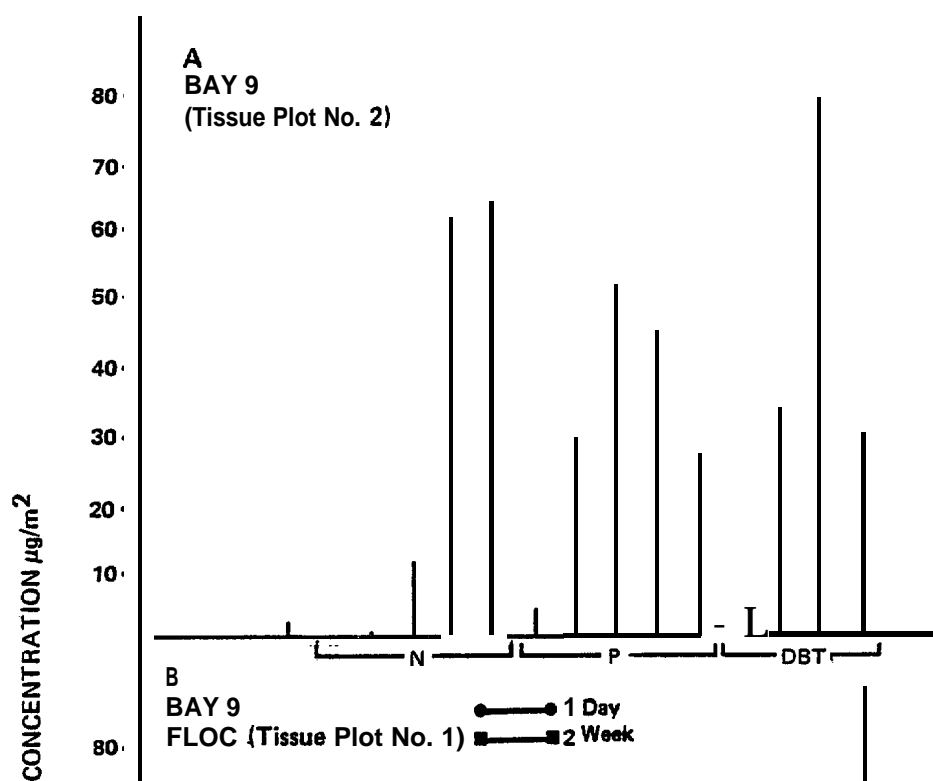
Figure 3.51. Aromatic Hydrocarbon Composition of Sediment F LOC Samples.

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statistically different from each other and significantly lower than the concentrations found at the **tissue** plots. However, data from both the tissue plots and the biology stations indicate that post-spill levels of petroleum were at least a factor of 10 greater than **pre-spill** levels, and that the concentrations of **oil in** Bay 9 sediments were at least 2 to 3 times **higher** than values found **in** Bay 10.

3.2.1.3.b Oil Composition by·GC^2

Two types of sample groupings from Bay 9 biological stations were analyzed by GC2.   Sediment from several **individual** sampling **points** along the **150m-long** depth stratum were analyzed separately.   In addition, sample extracts from each station (a station being comprised of **five** sampling points) were pooled to yield 1 GC^2 result (3 per depth stratum).   The relevant GC^2 parameters are summarized **in** Table 3.12.   Only the second post-spill sample set was subjected to GC^2 analysis.

As shown previously (Section **3.2.1.1.b),** the **PRIS/PHY** ratio and CPI index (both GC^2 **data parameterizations) are** good indicators in these clean sediments of oil inputs. Where **PRIS/PHY** is less than 3.5 **and/or** where CPI is less than 3.5, oil is clearly present.   The phytane concentration is presented here as it has been shown that there is a correlation between phytane and **total oil concentrations (see section 3.2.6). Phytane** concentrations greater than 0.005 **µg/g,** indicate the presence of petroleum as well.

The Bay 9 results clearly indicate that **oil is** present **in** the Bay 9 (second post **spill)** sediments.   Note how the phytane results correlate well **with** the **UV-determined** concentrations (see section 3.2.6 and **Figure** 3.44).   The

TABLE 3-12

SEDIMENT HYDROCARBON SOURCE SUMMARY:
GC^2 RESULTS - BIOLOGY STATIONS
(2nd POST-SPILL SAMPLING)

SAMPLE (BAY/DEPTH (m))	LOCATION[a]	PHYTANE (ppm)	PRIS/PHY	CPI	STATUS
9/3	2 0m	0.027	1.4	2.0	Oil
9/3	140m	0.029	2.8	2.2	Oil
9/7	20m	0.020	2.2	2.3	Oil
9/7	150m	0.072	1.6	2.2	Oil
9/3	(0-50m)	0.010	2.0	2.6	Oil (low)
9/3	(60-100m)	0.040	1.5	1.6	Oil
9/3	(110-150m)	0.050	2*2	2.8	Oil
9/7	(0-50m)	0.040	1.3	1.8	Oil
9/7	(60-100m)	0.030	1.5	2.0	Oil
9/7	(110-150m)	0.070	1.9	2.2	Oil
10/3	(0-50m)	0.008	2.6	3.4	Oil
10/3	(60-100m)	0.002	4.2	3.7	?
10/3	(110-150m)	0.005	5.4	4.1	?
10/7	(0-50m)	0.005	2.0	4.3	Oil
10/7	(60-100m)	0.002	2.0	4.5	Oil
10/7	(110-150m)	0.007	2.0	4.3	Oil
7/3	(0-50m)	0.002	12	5.0	No Oil
7/3	(60-100m)	0.001	30	4.5	No Oil
7/3	(110-150m)	0.002	26	5.8	No Oil
7/7	(0-50m)	0.001	7.0	9.0	No Oil
7/7	(60-100m)	0.001	5.0	6.5	No Oil
7/7	(110-150m)	0.002	6.0	6.8	No Oil
11/3	(0-50m)	0.008	3.0	3.1	No Oil
11/3	(60-100m)	0.002	3.5	3.0	No Oil
11/3	(110-150m)	0.008	4.1	4.9	No Oil
11/7	(0-50m)	0.016	1.4	2.6	Oil
11/7	(60-100m)	0.012	1.3	2.4	Oil
11/7	(110-150m)	0.019	1.6	2.4	Oil

aSee Figure 2.6.

low PRIS/PHY and CPI ratios are strong indications of the presence of oil in these samples as well. The phytane values (i.e., oil) in the Bay 9 biology station composites agree well with the individual station values (Table 3-12). For example, the 9/3 (110-150m) sample (0.05 ppm) agrees well with an individual sampling point within this station (9/3 - 150m; 0.07 ppm).

The oiled sediment samples are all of relatively low concentrations, as the background biogenic assemblage, though now of secondary importance, is still obvious on the GC2 traces (see Figure 3.45). The oil in the sedimentsis substantially weathered physico-chemically(i.e., loss of more soluble/ volatile, low-molecular weight, saturated and aromatic components), but shows no evidence of microbial degradation.

3.2.1.4 Microbiology Plots (Sediments) - Bay 9

3.2.1.4.a Oil Concentrations by UV/F

Bottom sediment samples were collected from two micro-biology stations in all four bays at approximately weekly intervals from August 9 to September 18, 1981. These sta-tions were located at the ten meter depth contour directly offshore from the north and south ends of the biological transects. Samples were collected from the Bay 9 stations, H5 and H6, on August 8 and 18 before any spills, on August 23 four days after the surface oil spill, before the dispersed-oil spill, and on August 30 and September 5, 13 and 18 after the dispersed oil spill. The samples were collected by divers using the same techniques as used for collecting sediments from the tissue plots and biology transects.

TABLE 3-13

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY UV/F IN
SEDIMENTS FROM THE MICROBIOLOGY STATIONS IN BAy 9 (µg/g)

STATION	AUG 8	AUG 14	AUG 23	AUG 30	SEP 5	SEP 12	SEP 18
			SAMPLING DATE				
H5	0.36	0.37	0.46	4.4	2.8	5.4	2.4
H6	0.51	0.28	0031	3.6	6.2	10.6	3.4

The concentrations of hydrocarbons (petroleum equivalents) as measured by UV/F ranged from 0.3 to 0.5 µg/g dry weight prior to the dispersed oil spill and increased by roughly an order of magnitude (.2 - 11 µg/g) following the dispersed oil spill (Table 3-13; Figures 3-42 through 3-44). There are no obvious temporal trends at the two stations nor is there a significant difference between the concentrations of oil found at the two stations following the spill. In summary, oil concentrations in Bay 9 were uniformly elevated by an order of magnitude following the dispersed oil spill.

3.2.1.4b Oil Composition by GC^2

A set of samples from the Bay 9 microbiology stations (H_5, H6) from August 18 (pre-spills), August 30, and September 5, 12, and 18 were analyzed by GC^2. The results are typical of surface sediments. Pre-spill compositions reflect a combination of marine and terrigenous biogenic inputs (See Figure 3-45). Analyses from both stations from August 30 and September 5 reveal low levels of oil, as evidenced by a smooth n-alkane distribution from $n-C_{14}$ to $n-C_{24}$. The CPI and pristane/phytane parameters clearly reveal the presence of oil in these low level pristane sediments (Table 3-14), as does the absolute level of phytane. The CPI is normally in the 5 to 10 range indicating a marked odd chain predominance and since pristane, the biogenic isoprenoid, is far more abundant than phytane (of petrogenic origin), the background pristane/phytane ratio is high, varying seasonally from 5 to 100. As even small additions of oil introduce phytane and even-chain n-alkanes (C_{20} to C32),the lowering of the CPI to less than or equal to 3.5 and/or the lowering or pristane/phytane to less than or equal to 3.5 signifies the presence of oil. The "no oil" to "oil" transition as revealed by these GC^2 parameters is shown in Table 3-14.

TABLE 3-14

SEDIMENT HYDROCARBON SOURCES BY
GC^2 (MICROBIOLOGY SEDIMENTS)

SAMPLE			PHYTANE (µg/g)	PRIS/PHY	CPI	STATUS
Bay 9						
	H5	8-30-81	.12	1.1	1.7	Oil
		9-5-81	.096	1.8	2.6	Oil
		9-18-81	.005	1.0	2.9	Oil
	H6	8-18-81	nd	40	7.6	No oil
		8-30-81	.11	0.9	2.1	Oil
		9-5-81	.091	1.7	3.2	Oil
		9-12-81	.069/.036	1.6/1.1	2.6/2.8	Oil
		9-18-81	.031	1.5	4.0	Oil
Bay 10						
	H4	8-14-81	nd	28	7.9	No oil
		8-30-81	.11	1.4	3.5	Oil
		9-5-81	.068	1.6	3.2	Oil
		9-12-81	.009	2.9	4.8	Low oil
		9-18-81	.016	2.4	5.0	Oil
Bay 11						
	H2	8-14-81	nd	~100	7.5	No oil
		8-30-81	.012	1.3	3.4	Oil
		9-12-81	.028	1.9	6.2	Low oil
		9-18-81	.023	1.2	3.3	Oil
Bay 7						
	H7	8-16-81	nd	>20	9.9	No oil
		8-31-81	.003	10	9.7	No oil
		9-13-81	.016	5.7	6.9	Low oil
		9-18-81	.007	22	9.3	No oil
Oil			--	0.75	1.0	--
Baseline Sediment			.001-.003	5-1oo	5-1o	--
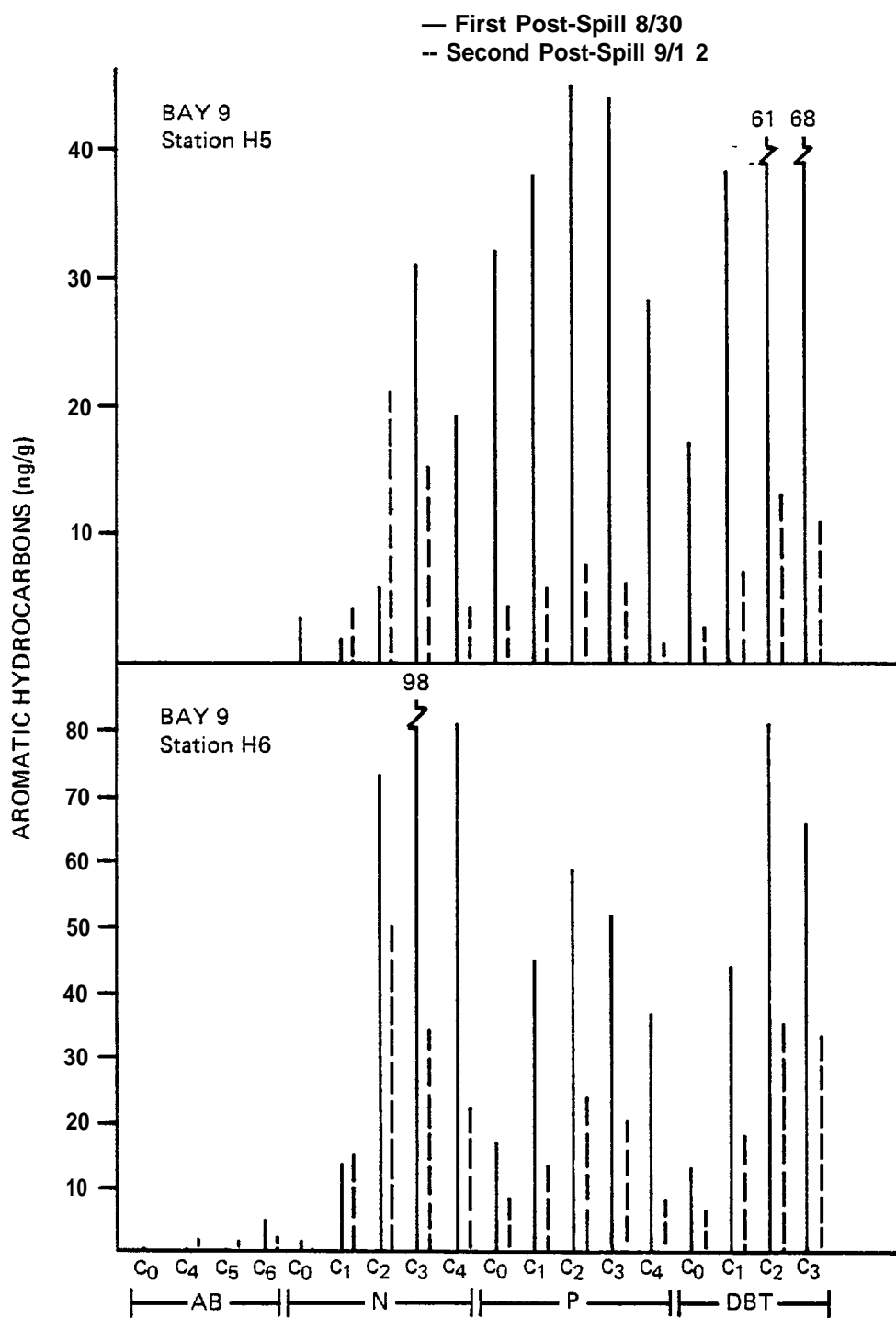
Figure 3.52. GC²/MS Resu Its from Sediment Microbiology Plots.

3.2.1.4c <u>Aromatic Hydrocarbon Composition by GC^2/MS</u>

A set of BAY 9 sediment samples from both microbiology stations, H5 and H6, from August 20 and September 12 were analyzed by GC^2/MS. The results are presented in Figure 3.52. According to these results individual aromatic hydrocarbon levels were generally in the 10-100 ppb range initially and dropped to the 2-50 ppb range two weeks later. However, a very similar composition including the full series of **napththalene,** phenanthrene and dibenzothiophene compounds was observed at both times. Those results are somewhat in contrast to those from the Bay 9 tissue plots (Figure 3.47) in which the aromatics were found at substantially lower quantities (2-5 ppb) and in which the sedimented oil appeared to weather over the two week post-spill period (i.e., loss of naphthalenes). Apparently a greater amount of "fresher" oil still persists in the benthic system, perhaps residing seaward of the 7 meter depth stratum (i.e., 10 meter **micro-** plots and seaward).

3.2.2 <u>Bay 10</u>

3.2.2.1 <u>Tissue Plots (Sediments) - Bay 10</u>

3.2.2.1a <u>Oil Concentrations by UV/F</u>

Sediment samples were obtained from the tissue plot stations of Bay 10 on August 14 **(prespill),** August 29 (+2 days from the dispersal oil spill) and September 11 **(+15** days from the spill). Concentrations of oil in **sedi-** ments rose from negligible **pre-spill** values (Figure 3.53) (7m: 0.49 **[.16,** .921, **3m:** 0.45 **[.32,** .59] µg/g)to approximately 1.0 µg/g for both of the post-spill samplings (Figures 3-54,
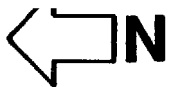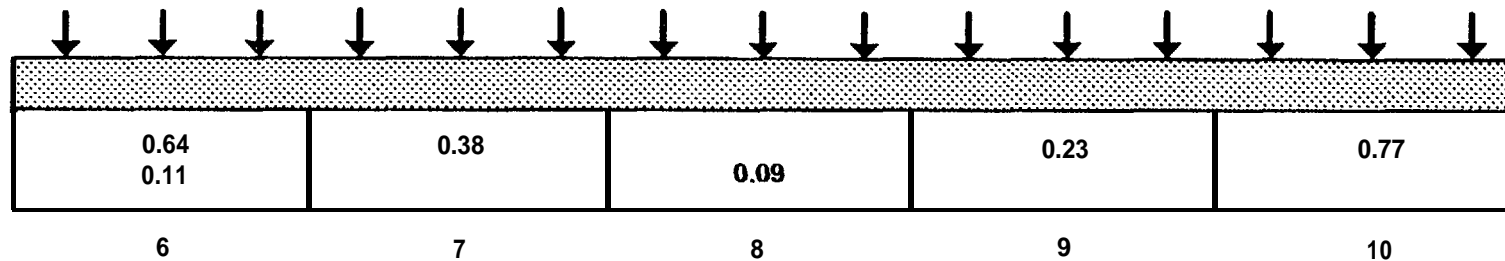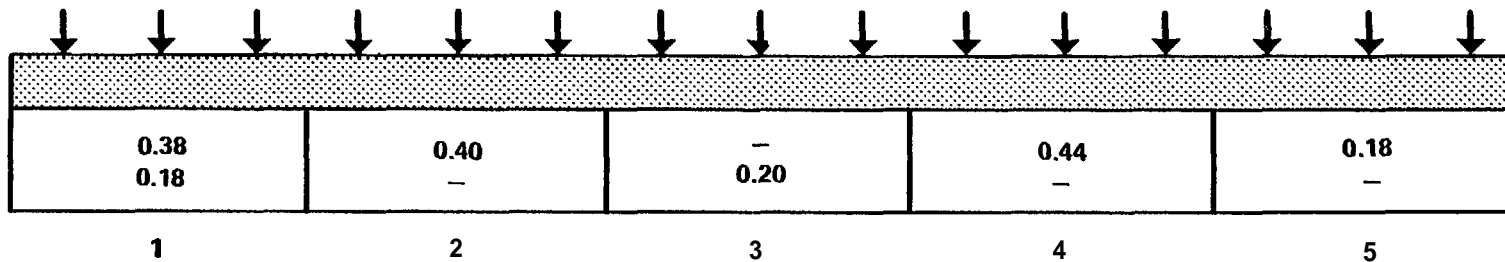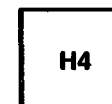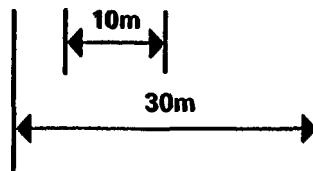
Figure 3.53. Oil Concentrations in sediments& Floe by UV/F (Bay 10—Prespill).
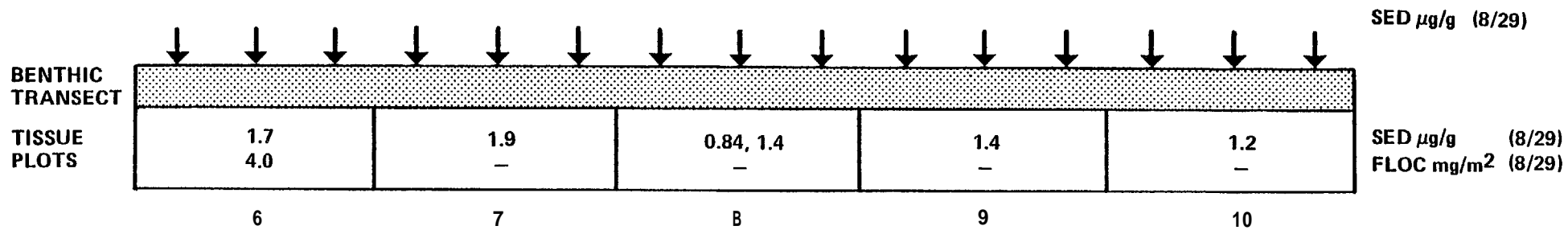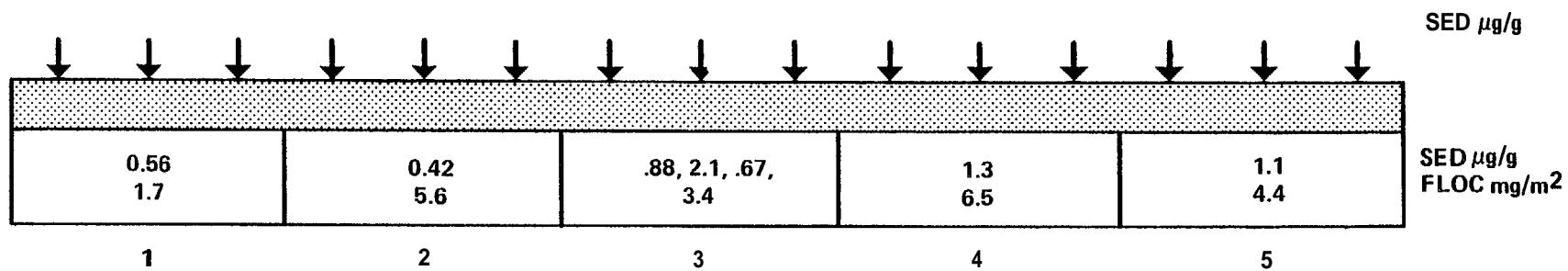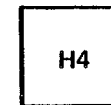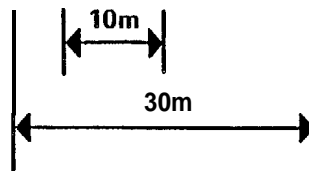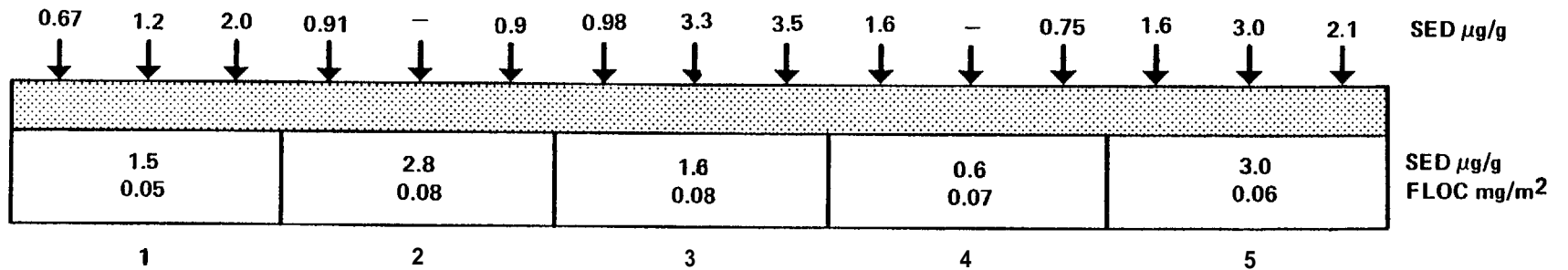
Figure 3.54. Oil Concentrations in Sediments& Floe by UV/F (Bay 10—1st Postspill).
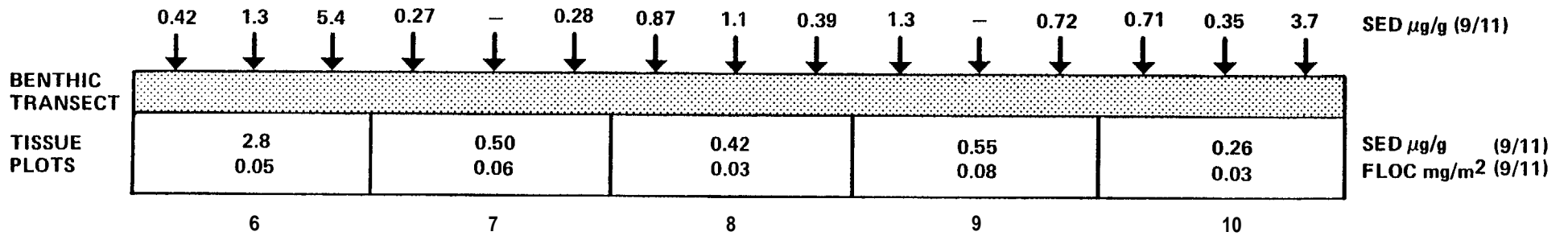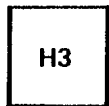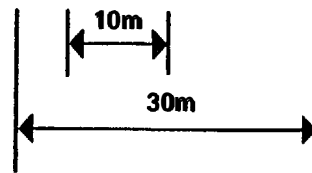
Figure 3.55. Oil Concentrations in Sediments& Floe by UV/F (Bay 10–2nd Postspill).

3-55). In contrast to those of Bay 9, concentrations of petroleum in the sediments of Bay 10 were quite variable ranging from 0.5 to 3 **µg/g.** This observed heterogeneity suggests that the contamination of sediments in Bay 10 was quite patchy. Only the second post-spill sampling of the 7m depth stratum and the first post-spill sampling of the 3m depth stratum differed statistically from the **prespill** sampling (see Appendix A). The 3m and **7m** depth strata were indistinguishable from each other during all samplings.

3.2.2.1b Oil Composition by GC ^{2}

GC^2 results from Bay 10 can be evaluated as previously mentioned for Bay 9 sediments. The results in Table 3-9 indicate the lesser relative impact of oil to Bay 10 sediments by virtue of a lesser lowering of the key ratios. Though oil is clearly observed in the GC^2 traces in all but one of the samples, the diagnostic ratios at Station 1 are borderline on their own. Oil is absent at Station 3 and clearly present by visual GC and all diagnostic ratios at Stations **5, 6,** and 10.

3.2.2.1c Aromatic Hydrocarbon Composition by GC 2/MS

Three samples from Bay 10 sediment tissue plots were examined by GC^2/MS. Low levels of aromatic hydrocarbons were observed immediately following the spill and similar quantities two weeks later (Figure 3.56). This corresponds with the **UV/F** trends which indicated similar oil levels during both samplings in this bay. The typical weathered oil aromatic profile is seen in the results (Figure 3.56).
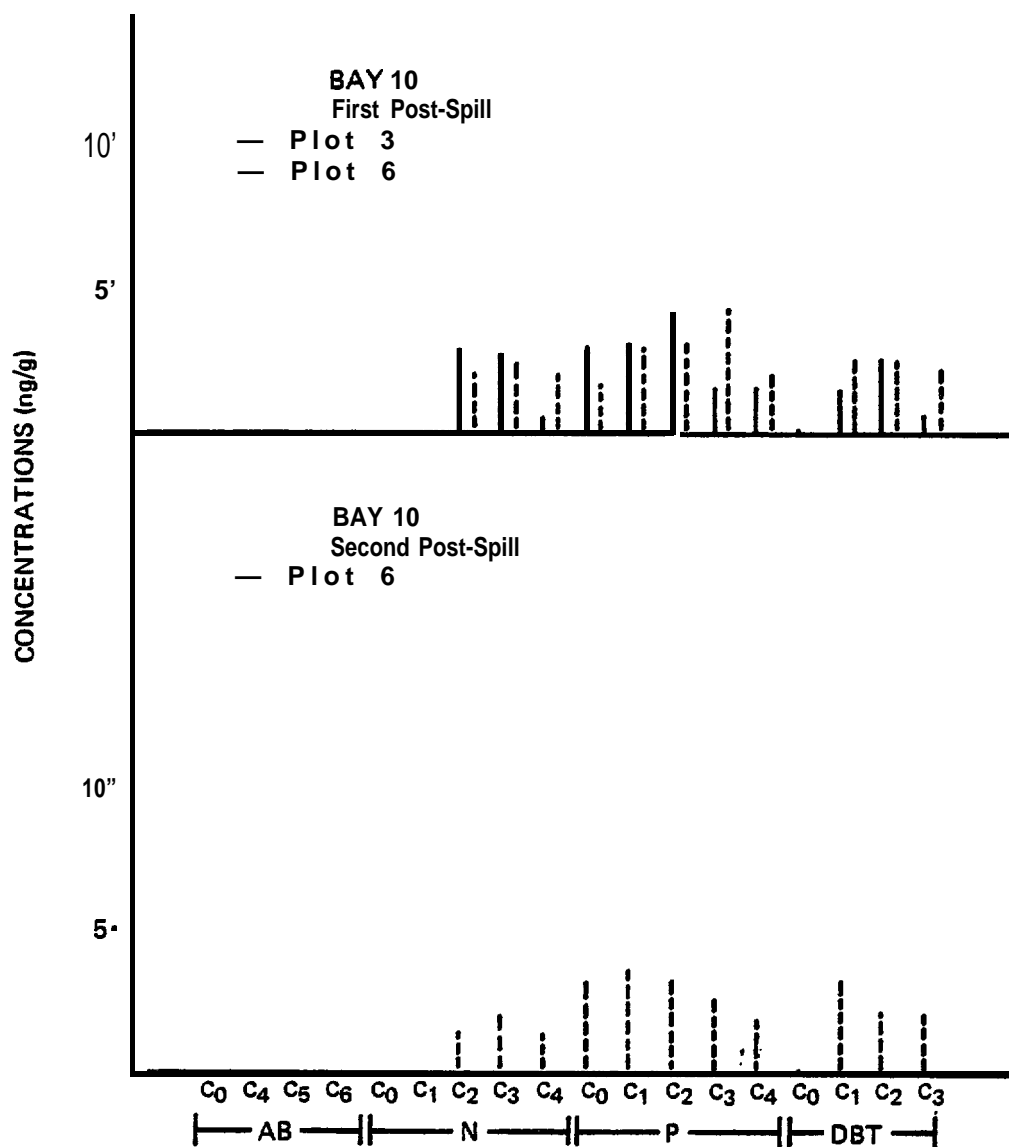
Figure 3.56. Bay 10 Sediment Tissue Plot Aromatic Hydrocarbons by GC^2/MS.

3.2.2.2 Tissue Plots (Floe) - Bay 10

3.2.2.2a Oil Concentrations by UV/F

Floe samples were collected from the tissue plots of Bay 10 on August 14 (pre-spill), August 29 (+2 days from the dispersed oil spill) and September 11, 1981 (+15 days from the dispersed oil spill). Samples from Stations 6 to 10 were not collected during the first post-spill sampling due to an equipment failure. The concentrations of hydrocarbons (petroleum equivalents) were low (<.15 mg/m^2) in both the pre-spill and second post-spill samplings and significantly elevated (7 m: 4.0 [2.0, 7.2] during the first post-spill sampling (Table 3-15, Figures 3-53 through 3-55). Using the conversion factor derived previously (Section 3.2.1.2.a), the floe contains approximately 20 percent of the oil in the bulk sediment during the first post-spill sampling and less than 1 percent during the second post-spill sampling.

In all respects, the input of petroleum to the surface floe from Bay 10 is similar to that from Bay 9. The absolute concentrations in Bay 10 floe are not statistically different from those in Bay 9 for the post spill samplings. The UV/F spectra are quite similar to those illustrated for Bay 9. As with Bay 9, the dispersed oil which entered Bay 10 immediately following the dispersed oil spill, sedimented into the floe layer and was completely incorporated into the bulk sediment and/or transported out of the bay within 2 weeks of the spill.

3.2.2.2b Oil Composition by GC^2 (floe)

Of the three samples of Bay 10 floe that were analyzed by GC^2, all were from the 1 day post-spill sampling. Low

TABLE 3-15

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY
UV/F IN SEDIMENT AND FLOC OF BAY 10

BAY	SAMPLING	STATION	FLOC (mg/m^2)	SEDIMENT (μg/g)	$\frac{FLOC}{SEDIMENT}$[1]
	Prespill	1	0.18	0.38	
		2		0.40	
		3	0.20		
		4		0.44	
		5		0.18	
		6	0.11	0.64	
		7		0.38	
		8	0.09		
		9		0.23	
		10		0.77	
	1st post spill	1	1.7	0.56	15%
		2	5.6	0.42	67%
		3	3.4	1.2	14%
		4	6.5	1.3	25%
		5	4.4	1.1	20%
		6	4.0	1.7	12%
		7			
		8			
		9			
		10			
				Average	26%
	2nd post spill	1	0.05	**1.5**	'1%
		2	**0.08**	**2.8**	'1%
		3	**0.08**	**1.6**	'1%
		4	0.07	0.6	'1%
		5	0.06	3.0	'1%
		6	0.05	2.8	`1%
		7	0.06	0.50	`1%
		8	0.03	0.42	'1%
		9	0.08	0.55	'12
		10	0.03	0.26	'12
				Average	'1%

[1]The floe/sediment ratio assumes a conversion equation
of floe (mg/m^2) x 0.05 = sediment (μg/g). See text for the
derivation of the factor.

levels of heavily weathered (SHWR = 1.1-1.4) saturated hydrocarbon residues were detected in all samples. GC^2 traces of aromatic fractions indicated only very small quantities of three-ringed aromatics (estimated to be 10-30 $\mu g/m^2$ of total three-ringed aromatics) in the samples. No evidence of biodegradation of any **sedimented** residues is observed. No GC^2/MS analyses *were* performed on Bay 10 floe samples.

3.2.2.3 Biology Stations - Bay 10

3.2.2.3a Oil Concentrations by UV/F

Sediment samples from the biology stations of Bay 10 were collected on August 29 (+2 days) and September 11 (+15 days) following the dispersed oil spill. Only samples from the second post-spill sampling were analyzed. Levels of petroleum at stations along the 7-m stratum (1.6 [1.1, 2.21 $\mu g/g$) are significantly higher than levels at stations along the 3-m transect (0.99 [.48, 1.71 $\mu g/g$) (Figure 3-55). A similar difference between the two sampling depths was not noted at the tissue plots. The concentrations of petroleum at biology stations and tissue plot stations were statistically different at the 7 m depth stratum but not at the 3 m depth stratum.

3.2.2.3.b Oil Composition by GC^2

The GC^2 parameters (Table 3-12) for Bay 10 sediments indicate that oil is present in the 7-meter stratum (all stations), but its presence cannot be unequivocally demonstrated by GC^2 in all of the points along the inshore (3m) stratum. Note how the **PRIS/PHY** ratio remains a good indicator

($\cong$ 2.0) in the 7-meter samples, but begins to fail in the 3-meter samples (PRIS/PHY = 4.2, 5.4). While suggesting the presence of oil in the 3-meter samples, the biogenic influence is great. The biogenic influence affects the CPI in all Bay 10 samples where now no values less than 3.4 (the borderline oil indication) are seen. This again demonstrates that where levels of oil are low the CPI is less useful than the PRIS/PHY ratio. Absolute phytane values are only slightly above background levels.

Thus, low incremental additions of oil are best seen by a cumulative property measurement such as UV/F. The response of UV/F is to a combined oil property rather than to individual components as is the case with GC2 and GC^2/MS. As individual components are 1-2 percent each of the total oil by weight, it is not surprising that UV/F can detect oil while GC2, GC^2/MS results may be ambiguous (at very low levels).

3.2.2.4 Microbiology Plots (Sediments) - Bay 10

3.2.2.4.a Oil Concentrations by UV/F

Sediment samples were collected from the two micro-biology stations, H3 and H4, in Bay 10 on August 9 and 14 prior to the oil spills, on August 23 following the surface oil spill and on August 30 and September 5, 12, and 18 following the dispersed oil spill. Concentrations of hydro-carbons (petroleum equivalents) were low (0.2 to 0.8 µg/g) prior to the dispersed oil spill and increased by a factor of five subsequent to the dispersed oil spill (Table 3-16; Figures 3-53 through 3.55). Whereas concentrations of oil in Bay 9 sediments remained uniformly high following the spill, those in Bay 10 showed a wide variability. Several values

TABLE 3-16

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY UV/F IN
SEDIMENTS FROM THE MICROBIOLOGY STATIONS IN BAy 10 (μg/g)

| STATION | SAMPLING DATE | | | | | | |
	AUG 8	AUG 14	AUG 23	AUG 30	SEP 5	SEP 12	SEP 18
H3	0.75	0.48	0.19	2.0	0.77	0.82	2.7
H4	0.54	0.78	0.14	5.5	1.3	0.53	1.10

at both stations fall within the range of concentrations found before the spill. The sediments at the microbiology stations in Bay 10 exhibit transient events of contamination which probably result from heterogeneity of the sample population which was also observed in the sediments sampled at the tissue plot and biology transect stations.

3.2.2.4b Oil composition by GC [2]

The same considerations and criteria that applied to Bay 9 sediments apply to Bay 10 as well. The data from Table 3-14 clearly illustrates the input of oil to Bay 10 microbiology sediments with some small qualitative change in the post-spill period seen, as evidenced by the increasing PRIS/PHY and CPI values corresponding to a decrease in absolute phytane levels (i.e., decreasing levels of oil).

3.2.3 Bay 7

3.2.3.1 Tissues Plots (Sediments) - Bay 7

3.2.3.1a Oil Concentrations by UV/F

Surface sediment was sampled from the tissue plot stations of Bay 7 on August 17 (prespill), August 31 (+4 days from the dispersed oil spill, +16 days from the surface oil spill) and September 10 (+14 days from the dispersed oil spill, +26 days from the surface oil spill). The mean concentrations of "oil equivalents" in the surface sediments were low (less than 0.6 µg/g) for all three samplings (Figures 3.57-3.59). Although the mean concentration of petroleum for the second postspill sampling was low, isolated stations
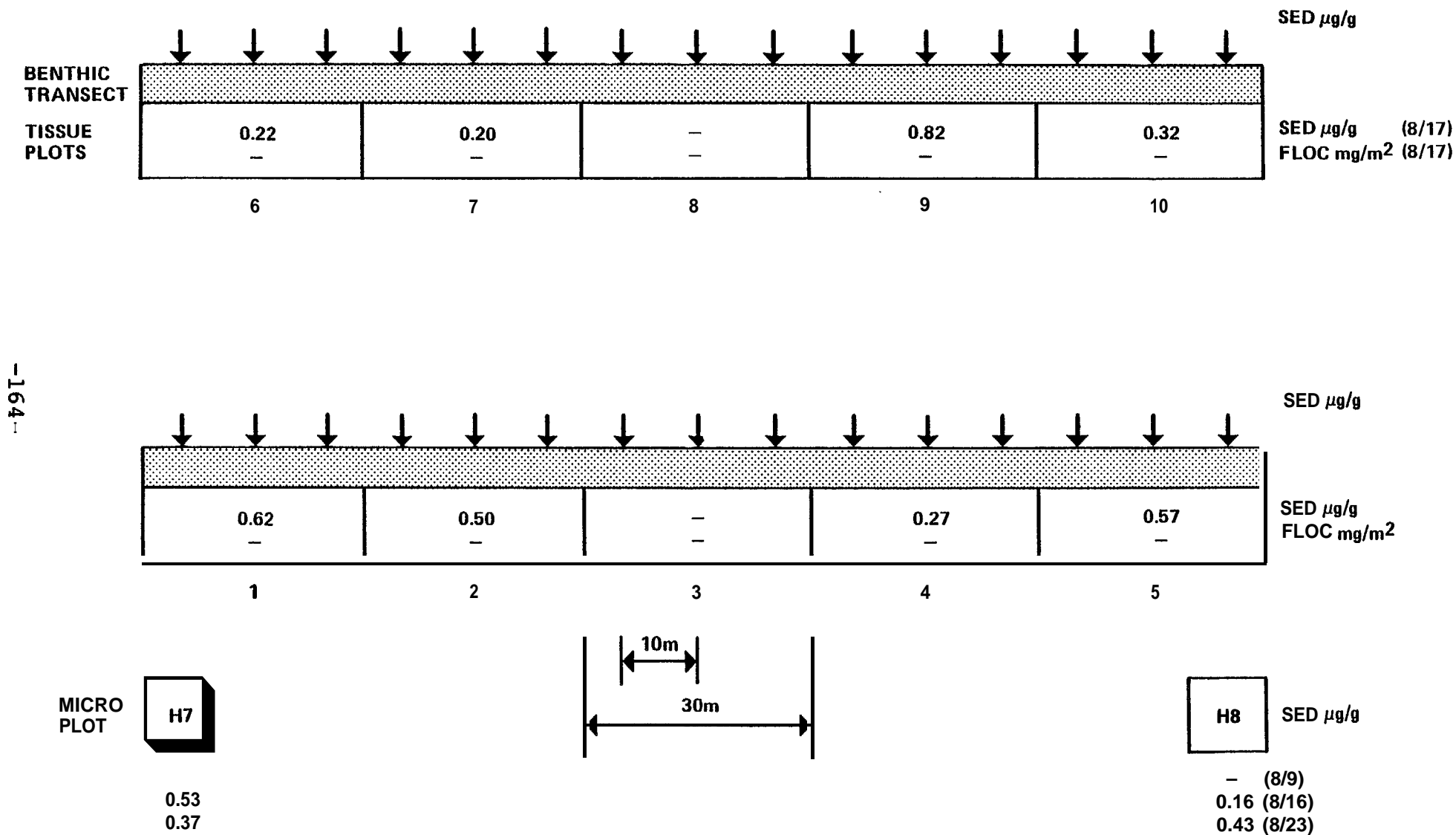
Figure 3.57. Oil Concentrations in Sediments & Floe by UV/F (Bay 7—Prespill).
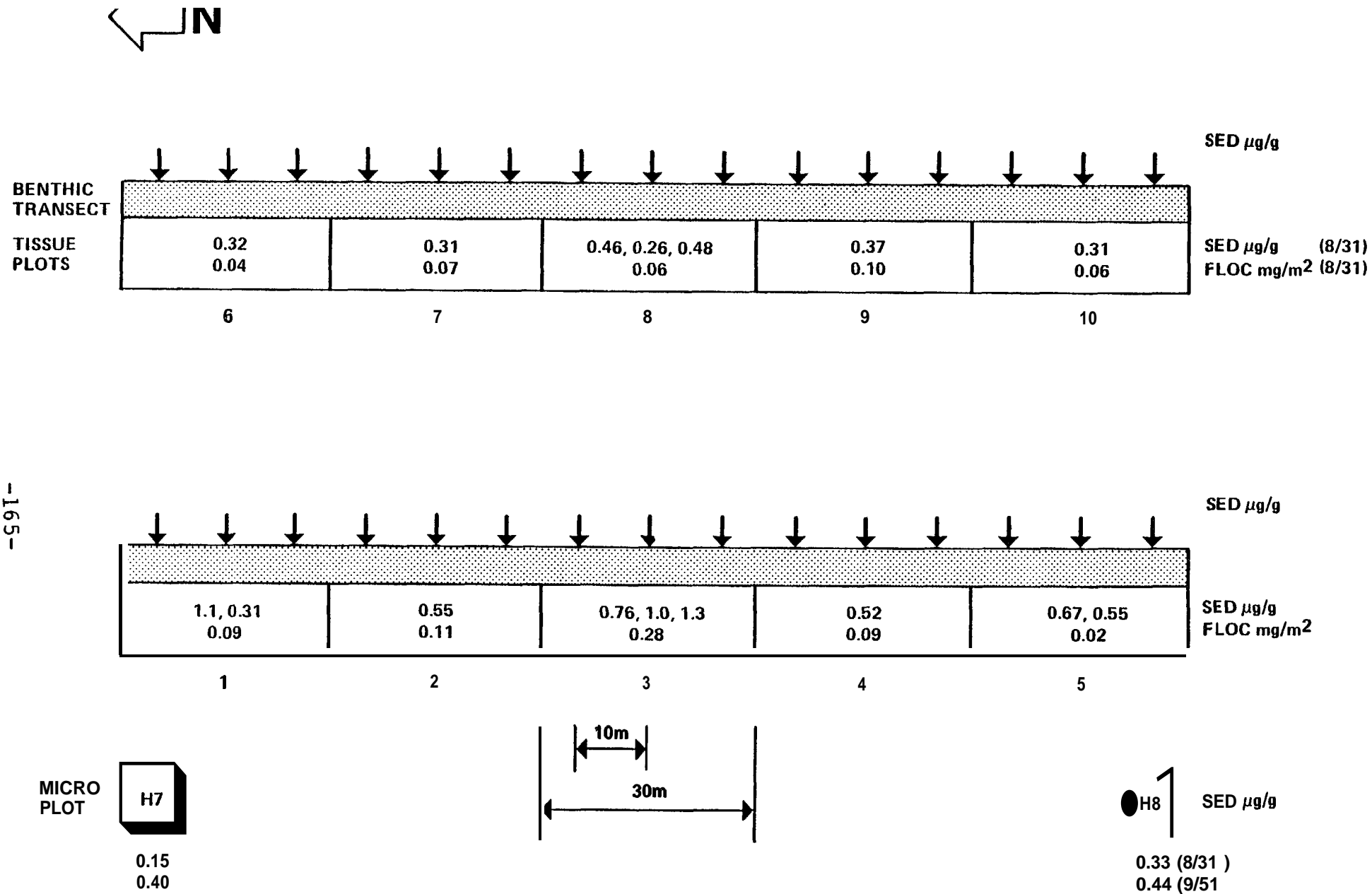
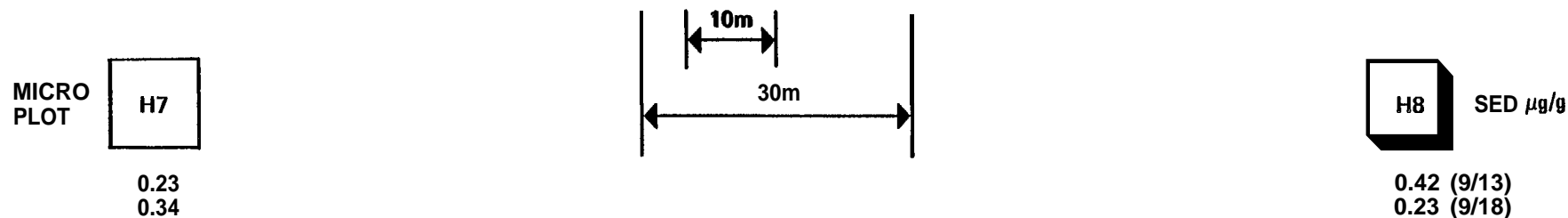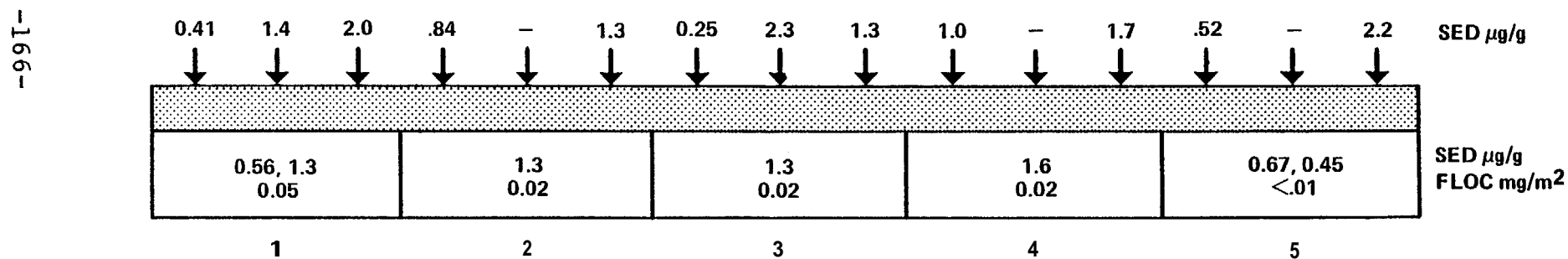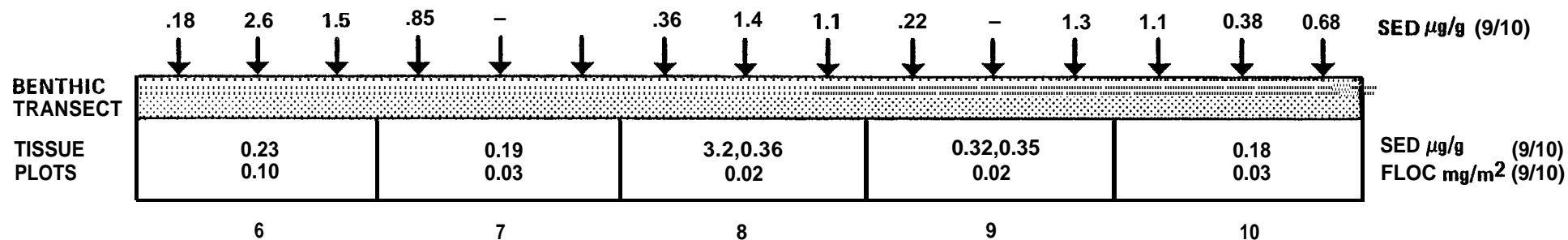Figure 3.58. Oil Concentrations in Sediment& Floe by UV/F (Bay 7—1st Postspill).

Figure 3.59. Oil Concentrations in Sediments & Floc by UV/F (Bay 7–2nd Postspill).

showed elevated (greater than 1 µg/g) levels of petroleum.
These stations may be slightly contaminated with petroleum
from the dispersed oil spill.

3.2.3.1b Oil Composition by GC[2]

Oil was detected in very low levels in one of the
seven sediment samples analyzed (Plot 4; 7 meters; 2nd post
spill). Of the other samples, high pristane/phytane and CPI
values (see Table 3-9) persist and a smooth distribution of
n-alkanes in the C_{14}-C_{24} region are lacking. These findings
indicate that low levels of oil were present in the Bay 7
sediments, albeit in patchy occurrences. For the most
part the GC[2] data indicate that Bay 7 sediment oiling is a
minor factor in the post-spill benthic impact.

3.2.3.1c Aromatic Hydrocarbon Composition by GC[2]/MS

Of two samples analyzed (Figure 3-60, upper) only the
Co and C_1 phenanthrenes were detected at the 2 ppb level.
These compounds are present in pre-spill samples and samples
from the 1980 (baseline study) (see Figure 3-60 lower). The
detection of these compounds and the presence of four-ringed
aromatics (i.e., PAH) is indicative of a pyrogenic origin from
the global transport of fossil fuel combustion residues.

3.2.3.2 Tissues Plots (Floe) - Bay 7

3.2.3.2.a Oil Concentrations by UV/F

Floe was sampled from Bay 7 on August 31 (+4 days from
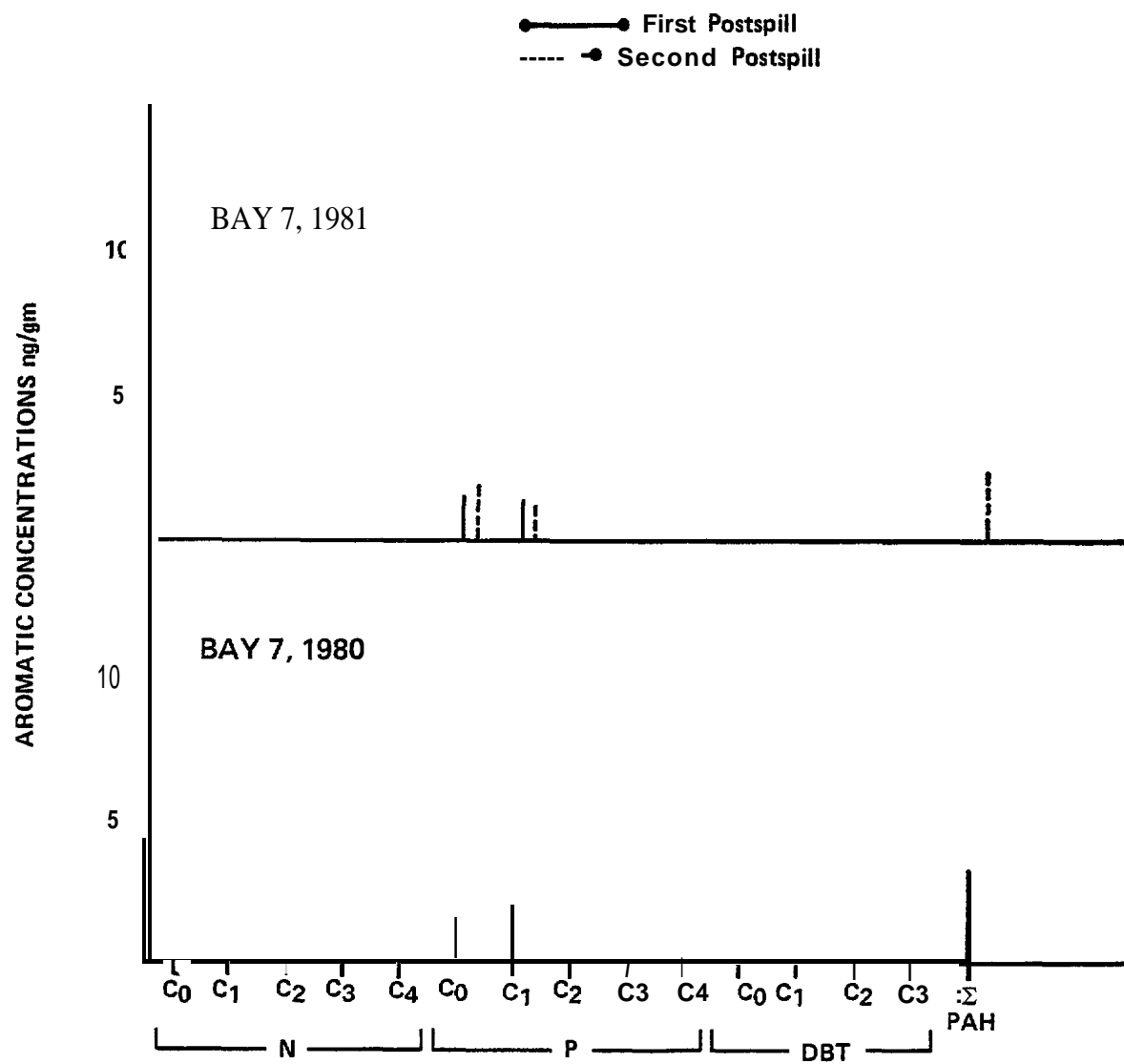the dispersed oil spill, +16 days from the surface oil

Figure 3,60, ·Bay 7 sediments (aromatic hydrocarbons) (GC^2/MS).

spill) and September 10, 1981 (+14 days from the dispersed
oil spill, +26 days from the surface oil spill). No floe
samples were collected prior to the surface oil or dispersed
oil spills. The concentrations of petroleum in the floe
were low (<0.1 mg/m^2) during both samplings (Figures 3-58,
3-59; Table 3-17). Although the concentrations in floe
collected during the first post-spill sampling are higher
than those for the second postspill sampling, the magnitude
of the difference is very small (.04 mg/m^2), and the difference
is not statistically significant. No contamination of the
Floe in Bay 7 was detected by UV/F. The magnitude of any
contamination would be more than two orders of magnitude
smaller than that observed in Bay 9 and Bay 10.

3.2.3.2b Composition of Oil by GC^2

Of the 4 floe samples subjected to GC^2 analyses
(Stations 1, 5 first post-spill; 1,5 second post spill), a
very small amount (∿0.5 ng/m^2) of saturated hydrocarbon
petroleum residue was found in one one-day sample (Station 1).
However, the GC^2 trace showed minute amounts of n-alkane
components. Thus we conclude that if oil is actually present
in the Bay 7 system it exists only during the period between
the dispersed oil spill and 4 days later (i.e., the first
postfill sampling) and only at questionably low levels.

3.2.3.2c Composition of Aromatics by GC^2/MS

Two samples were analyzed by GC^2/MS. The first postspill
sample analyzed contained trace (1 $\mu g/m^2$) levels of C_1, C_2, and
C3 phenanthrenes, similar to Bay 9, two-week levels (see
Figure 3-51). Aromatics were non-detectable in the two-week
post-spill sample.

TABLE 3-17

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY
UV/F IN SEDIMENT AND FLOC OF BAY 7

SAMPLING	STATION	FLOC (mg/m^2)	SEDIMENT ($\mu g/g$)	FLOC SEDIMENT[1]
Prespill			no data	
1st post spill	1	.09	.71	<1%
	2	.11	.55	1%
	3	.28	1.0	1%
	4	.09	.52	1%
	5	.02	.61	<1%
	6	.04	.32	1%
	7	.07	.31	**1%**
	8	.06	.40	1%
	9	.10	.37	1%
	10	.06	.31	1%
			Average	1%
2nd post spill	1	.05	.93	<1%
	2	.02	1.3	<1%
	3	.02	1.3	<1%
	4	.02	1.6	**<1%**
	5	<.01	.56	<1%
	6	.01	.23	<1%
	7	.03	.19	**1%**
	8	.02	.36	<1%
	9	.02	.50	<1%
	10	.03	.18	1%
			Average	1%

[1]The floe/Sediment ratio assumes a conversion equation
of floe (mg/m^2) x 0.05 = sediment ($\mu g/g$). See text for
the derivation of the factor.

3.2.3.3 Biology Stations - Bay 7

3.2.3.3a Oil Concentrations by UV/F

On August 31 (+4 days from the dispersed oil spill)
and September 10 (+14 days), sediments were collected from
stations along the biology stations in Bay 7. Only samples
from the second post-spill sampling were analyzed (Figure
3-59). Petroleum concentrations as measured by UV/F were
low at both the 3 m (0.80 [.45, 1.2] and the 7 m (1.2 [.77,
1.6] depth strata. No differences between concentrations
measured at the two benthic transects nor between concentrations
at biology station and tissue plots were apparent. As noted
in the tissue plot data, sporadically elevated concentrations
(greater than 1.0 µg/g) of petroleum were found during the
second post-spill sampling of the benthic transects. This
may suggest slight contamination of the sediments with oil
from the dispersed oil spill.

3.2.3.3.b Oil Composition by GC^2

GC^2 results indicate that oil is absent or present at
very low levels in Bay 7 sediments. Both PRIS/PHY and CPI
values (Table 3-12) are clearly biogenic and absolute levels
of phytane are at background levels. GC^2 traces all
resemble that in Figure 3.45 (bottom), which shows a purely
biogenic composition.

That there is some ambiguity in the analytical results
vis-a-vis oil/no oil determinations in this bay is evidenced
by the occasionally elevated UV/F values in these biology
stations (Figure 3.59) in the 1-3 ppm range with the corres-
ponding GC^2 data indicating "no oil" present. The mean

UV/F value for the O-50m station and that for the other
groupings is less than 1.3 ppm. Below this UV/F determined
value, GC^2 may not be able to discriminate minute quanti-
ties of oil from background. Indeed, this appears to be the
case in Bay 10 (**60-100m; 110-150m;** 3-meter depth) as well.
Thus, our conclusion must be that minute quantities of oil
are present in Bay 7 sediments which are only revealed by
UV/F results.

3.2.3.4 <u>Microbiology **Plots (Sediments) - Bay** 7</u>

3.2.3.4.a<u>Oil Concentrations by UV/F</u>

Samples of the bottom sediment were collected at
stations H7 and H8, the two microbiology stations in Bay 7,
on August 16 before the surface oil spill, on August 23
after the surface oil spill and on August 30 and September
5, 13 and 18 following the dispersed oil spill. No contamin-
ation of the sediments in Bay 7 is evident from the concen-
trations of petroleum equivalents measured by **UV/F.** Al 1
concentrations are uniformly low and range from 0.2 to 0.6
μg/g (Table 3-18). This observation is consistent with
concentrations of oil measured in water and in other sedi-
ments collected from Bay 7. Any traces of oil which reached
the sediment would be diluted by the uncontaminated material
collected from the top two centimeters of sediment and would
be very difficult to detect by this method. However, as we
have already shown, oil contamination of the surface floe
was negligible in this bay.

3.2.3.4b <u>Oil Composition by GC^2</u>

Four sediments from the microbiology stations at Bay 7
were analyzed by GC^2. Three of the samples were free

TABLE 3-18

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY UV/F IN
SEDIMENTS FROM THE MICROBIOLOGY STATIONS IN BAY 7 (µg/g)

	SAMPLING DATE						
STATION	AUG 8	AUG 14	AUG 23	AUG 30	SEP 5	SEP 12	SEP 18
H1		0.53	0.37	0.15	0.40	0.23	0.34
H2		0.16	, 0.43	0.33	0.44	0.42	0.23

of detectable oil as shown by the results in **Table** 3-14.
One sample taken from H7 on Sept. 13 showed a small amount
of oil reflected in the GC^2 data by increased phytane
levels and somewhat decreased **PRIS/PHY** and **CPI** values.   Note
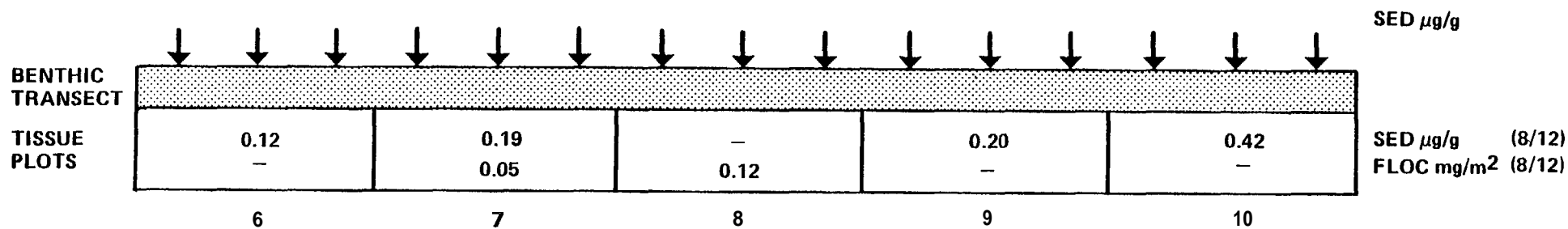however that the UV/F value of 0.23 ppm is of a background
magnitude.

3.2.4 Bay 11

3.2.4.1 Tissue Plots - Bay 11
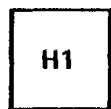
3.2.4.1a Oil Concentrations by UV/F

Sediments from the tissue plot stations of Bay 11 were
sampled on August 12 **(pre-spill),** August 21 **(+2** days from
the surface oil spill, 6 days before the dispersed oil
spill) and September 8 (+20 days from the surface oil spill,
+12 days from the dispersed oil spill).   Concentrations of
oil were uniformly low (less than ,0.7 **µg/g)** for both the
prespill and first post-spill sampling (Figures 3-61 through
3-63).   The slightly elevated (not statistically significant)
concentrations measured during the second post-spill
sampling suggest that the sediments may be **slighly** contam-
inated with petroleum.   As with Bay 7, isolated stations
have levels greater than 1 **µg/g** which probably suggest
heterogeneous contamination of Bay 11 sediments.

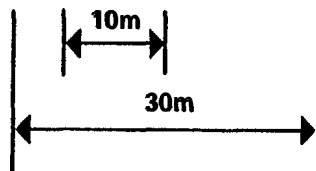### 3.2.4.1b Oil Composition by GC^2

No oil was detected in any first post-spill sampling.
However, in all of the second post-spill sampling, oil is
present (Table 3-9), as revealed by the diagnostic ratios
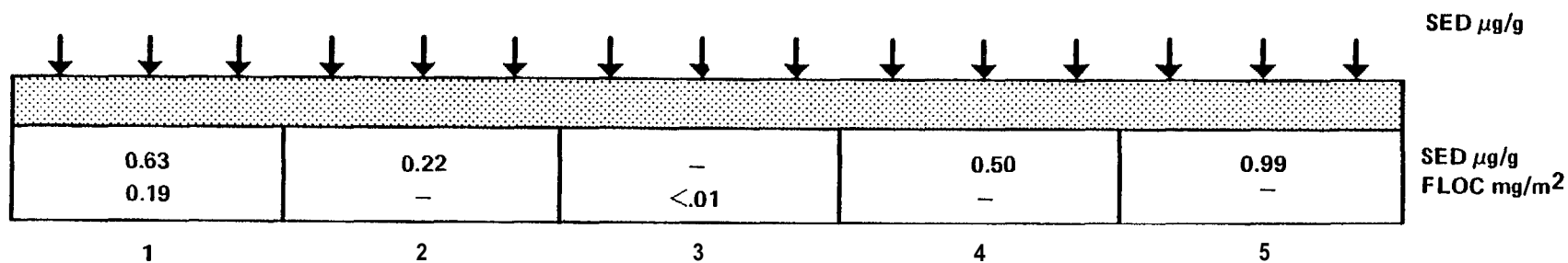
Figure 3.61. Oil Concentrations in Sediments& Floe by UV/F (Bay 1 1—Prespill).

IN

SED µg/g

BENTHIC
TRANSECT

TISSUE
PLOTS

0.16	0.29	0.13,.17,.41	0.08	0.04
6	7	8	9	10

SED µg/g   (8/21)
FLOC mg/m² (8/21)

SED µg/g

0.07 0.40	0.10 0.40	0.09,.72,.81 0.40	0.14 <.01	0.14 <.01
1	2	3	4	5

SED µg/g
FLOC mg/m²

|← 10m →|

30m

MICRO
PLOT   H1

0.20
1.9

H2   SED µg/g

0.52 (8/23)
0.40 (8/30)
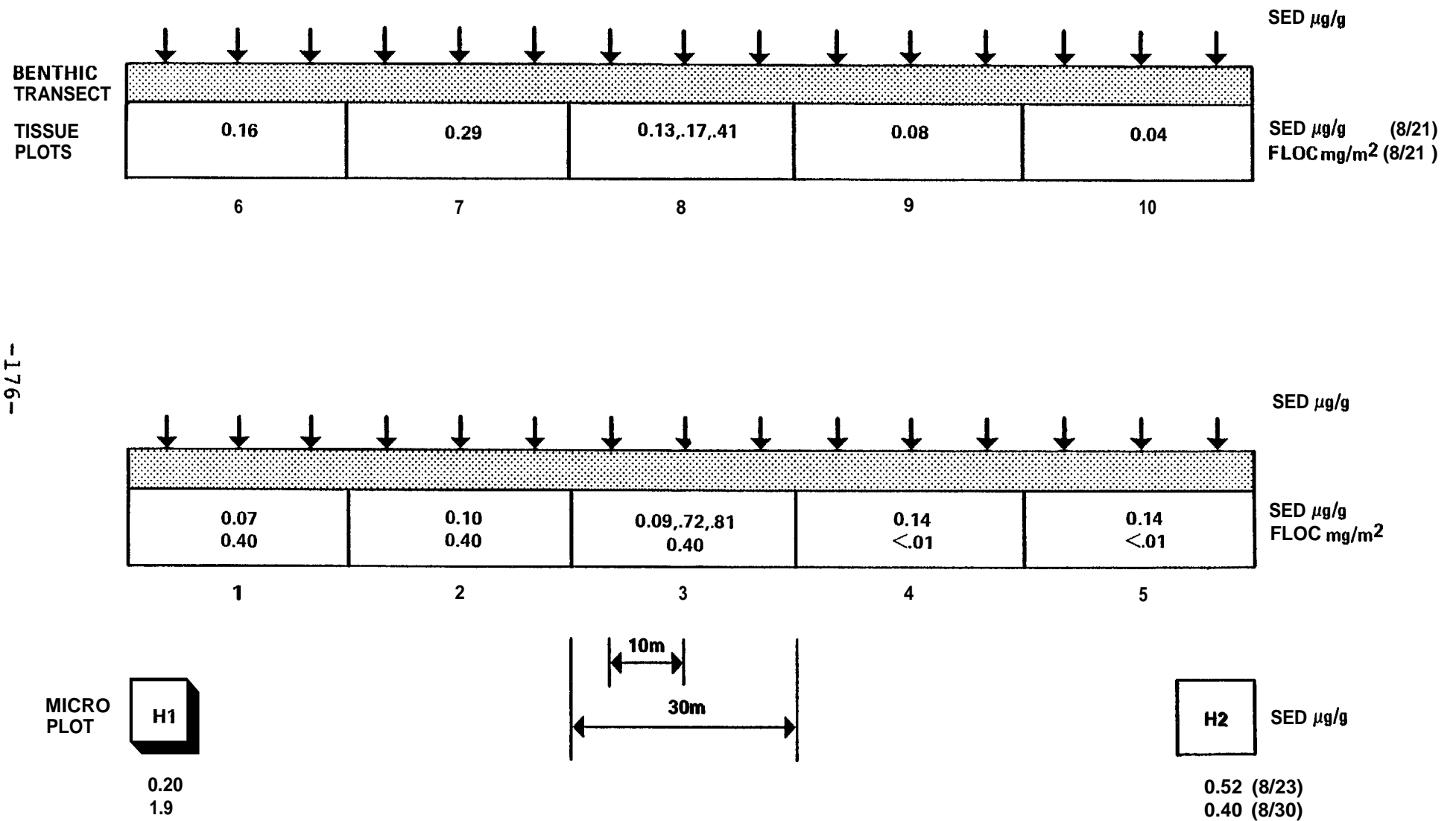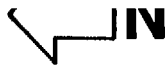
Figure 3.62. Oil Concentrations in Sediments and Floe by UV/F (Bay 1 1—1st Postspill).

Figure 3.63. Oil Concentrations in Sediments& Floe by UV/F (Bay 11–2nd Postspill).
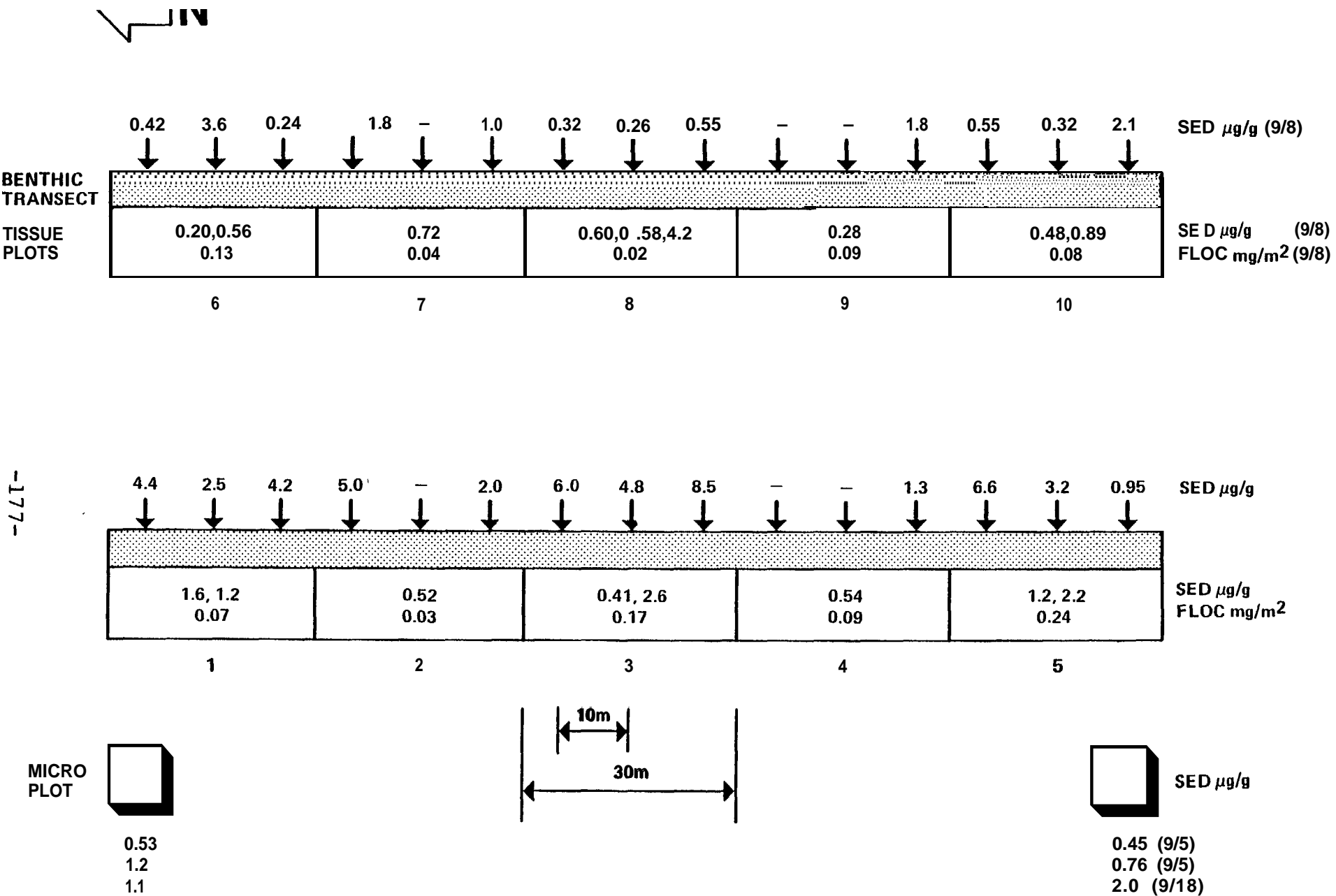
and the uniformity of the smooth $n\text{-}C_{14}$ to $n\text{-}C_{24}$ distribution. Oil found in Bay 11 sediments is nearly identical in its weathering state to that found in Bays 9 and 10.

3.2.4.1c Aromatic Hydrocarbon Composition by GC^2/MS

Of the one post-spill tissue plot sample analyzed (Figure 3-47), small amounts of **alkylated phenanthrene** and dibenzothiophene compounds were detected (1-2 ppb per individual compound) thus indicating the presence of a weathered petroleum aromatic assemblage.

3.2.4.2 Tissue Plots (Floe) - Bay 11

3.2.4.2a Oil Concentrations by UV/F

Samples of floe were collected from the tissue plots of Bay 11 on August 12 (pre-spill), August 21 (+2 days from the surface oil spill, 6 days before the dispersed oil spill) and September 8, 1981 (+20 days from the surface oil, +12 days from the dispersed oil spill). Floe from Stations 6 to 10 on the 3-meter transect could not be collected during the August 21 sampling due to a layer of surface oil within the boomed area. Floe from Stations 1 to 5 was collected from outside of the boomed area during this sampling.

The concentrations of hydrocarbons (petroleum equiva-lents) oil in the floe were low (less than 0.4 mg/m^2) and statistically similar to the prespill values during the two postspill samplings (Table 3-19). Three of the samples collected from Bay 11 during the first post-spill sampling contained minor amounts of petroleum which comprise 20 percent of the oil found in the bulk sediment. The remainder of the samples contained negligible absolute

TABLE 3-19

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY
UV/F IN SEDIMENT AND FLOC OF BAY II

SAMPLING	STATION	FLOC (mg/m^2)	SEDIMENT (µg/g)	FLOC SEDIMENT[1]
Prespill	1	.19	.63	
	2		.22	
	3	<.01		
	4		.50	
	5		.99	
	6	.05	.12	
	7		.19	
	8	.12		
	9		.20	
	10		.42	
1st post spill	1	0.40	.07	29%
	2	0.40	.10	20%
	3	0.40	.54	4%
	4	<.01	.14	<1%
	5	<.01	.14	<1%
	6			
	7			
	8			
	9			
	10			
			Average	11%
2nd post spill	1	.07	1.4	<1%
	2	.03	0.52	<1%
	3	.17	1.5	<1%
	4	.09	0.54	<1%
	5	.24	1.7	<1%
	6	.13	0.38	2%
	7	.04	0.72	<1%
	8	.02	1.8	<1%
	9	.09	.28	2%
	10	.08	.69	1%
			Average	<1%

[1]The floe/sediment ratio assumes a conversion equation
of floe (mg/m^2) x 0.05 = sediment (µg/g). See text for the
derivation of the factor.

quantities which comprised less than two percent of the oil found in the bulk sediments.

The floe in Bay 11 does not exhibit contamination from either the surface oil or dispersed oil spill. As with Bay 7, the levels of petroleum in Bay 11 during all sampling were two orders of magnitude lower than Bay 9 and Bay 10 during the first post-spill sampling. Due to the transient nature of contaminated floe as evidenced by results from Bays 9 and 10, the floe in Bay 11 could have been contaminated immediately following the dispersed oil spill and returned to an uncontaminated state before the second post-spill sampling. In contrast to floe in the bays associated with the dispersed oil spill, floe in Bay 11 was not contaminated immediately following the surface oil spill. This may have resulted from the lower levels of oil found in the water column during the surface oil spill compared to the dispersed oil spill and the lack of vertical mixing of oil in the top meter of water to the bottom (see Section 3.1).

3.2.4.2b Oil Composition by GC^2

No samples of Bay 11 floe were analyzed by GC^2. One sample was directly employed by GC^2/MS.

3.2.4.2c Aromatic Hydrocarbon Composition by GC^2/MS

One sample of the September 8 surface floe (second postspill) was analyzed to search for aromatic residues either being eroded from the Bay 11 beach or cross-contaminated from the dispersed oil spill. Evidence for neither was found since the GC^2/MS results yielded only small traces of phenanthrene residues, not necessarily related to any experimental oil spillages.

3. 2.4.3   Biology Stations (Sediments) - Bay 11

3.2.4.3a Oil Concentrations by UV/F

Surface sediment samples were collected from the two biology strata on August 21 (+2 days from the surface oil spill, 6 days before the dispersed oil spill) and September 8 (+20 days from the surface oil spill, +12 days from the dispersed oil spill). Samples from the second postspill sampling were analyzed for petroleum hydrocarbons by UV fluorescence. The stations along the 7-m stratum contained significantly higher concentrations of petroleum ($\bar{x}_G=3.5\pm2.0$ µg/g) than did stations along the 3-m stratum ($\bar{x}_G=0.72\pm.39$ µg/g) . This trend was present, but not as pronounced as in the tissue plot data. These data indicate that the offshore sediments, more so than the inshore sediments of Bay 11 are becoming slightly and heterogeneously contaminated with petroleum.

3.2.4.3.b Oil Composition by GC^2

The GC^2 results from Bay 11 biology stations indicate that the presence of oil is questionable in the two-week sampling at 3 meters, but is unambiguously present at 7 meters (Table 3-12). Again the PRIS/PHY and CPI values are on the oil/no oil borderline and visual scrutiny of the GC^2 reveals some n-alkane activity in the $C_{14}-C_{20}$ region. The parameter ratios (Table 3-12) plus the absolute phytane values shows that oil is more concentrated in the 7-meter stratum. This parallels the UV/F results (Figure 3.63), which indicate higher absolute oil levels at 7 meters. Oil levels in the 3-meter sediments are again in the $\sim$1.0-1.4 ppm range (the average of each station = five sampling points), which is at the low end of the GC^2 discrimination range.

3.2.4.4 Microbiology Plots (Sediments) - Bay 11

3.2.4.4a Oil Concentrations by UV/F

Bottom sediments were sampled at the microbiology
stations in Bay 11 on August 9 and 14 prior to the surface
oil spill, on August 23 three days after the surface oil
spill and on August 30 and Septebmer 5, 12 and 18 following
the dispersed oil spill. With the exception of four samples
collected in late August and early September, the concentra-
tions of petroleum equivalents measured by UV/F were at or
near background levels of 0.2 to 0.8 µg/g (Table 3-20). The
August 30, September 12 and September 18 samples at Station
H1 and the September 18 samples at Station H2 showed elevated
levels of petroleum (less than 1 µg/g). These data show
that the bottom sediments at the Bay 11 microbiology stations
remained relatively uncontaminated for two to three weeks
following the surface oil spill after which the levels of
petroleum increased slightly.

Although the UV spectra cannot be used to distinguish
oil derived from the surface spill from oil derived from the
dispersed spill, the delay of the appearance of uniformly
contaminated sediments until late on the sampling season
suggests that the oil is not associated with the dispersed oil
spill. The opportunity for direct sedimentation of dispersed
oil from the water, i.e., elevated levels of oil in the water
column, existed for only a few days after the dispersed oil
spill. Both Bay 7 and Bay 11 showed roughly equal levels of
petroleum in the water column following the dispersed oil spill
and neither (with the exception of Station H1 from August 30)
had elevated levels of oil in sediments for the two subsequent
samplings. The oil observed in Bay 11 sediments could have
been derived either from contaminated sediments transported

TABLE 3-20

CONCENTRATIONS OF PETROLEUM EQUIVALENTS BY UV/F IN
SEDIMENTS FROM THE MICROBIOLOGY STATIONS IN BAY II (μg/g)

	SAMPLING DATE						
STATION	AUG 8	AUG 14	AUG 23	AUG 30	SEP 5	SEP 12	SEP 18
H1	0.43	0.38	0.20	1.9	0.53	1.2	1.1
H2	0.24	0.70	0.52	0.40	0.44	0.76	2.0

from Bays 9 and 10, or more likely from oil-contaminated beach sediments transported offshore in Bay 11.

3.2.4.4b Oil Composition by GC[2]

No **oil** was detected in the August 14 **pre-spill** sample (**CPI=7.5,** pristane\phytane $\cong$ 100) (Table 3-12). However, the GC[2] traces from August 30 through September 12 clearly indicate the increasing presence of oil as noted by low levels of **n-alkanes** and isoprenoids in the C_{14} to C24 boiling range affecting the pristane\phytane ratio (1.2-1.9). Though there is not enough oil present in the Sept. 13 sample (Figure 3-64) to appreciably alter the strong terrigenous **n-alkane** fingerprint in the $n-C_{26}-n-C_{31}$ region and the CPI (Table 3-14), during September the CPI decreases as additional oil is eroded from the shoreline. Thus the visual GC[2] trace is needed to avoid a **false-**negative decision on the presence/absence of oil.

3.2.4.4c Aromatic Hydrocarbon Composition by GC[2]/MS

Evidence for the deposition of weathered oil at the south microbiology plot (**H2**) in Bay 11 is revealed through the aromatic hydrocarbon profile in Figure 3.65. A "sedimented oil profile indicating persistence of **alkylated phenanthrene, napththalene** and debenzothiophenes again forms the molecular marker profile in the sediments. Levels of individual phenanthrene compounds in the 1-10 ppb range are typical in those sediments, **slighty** higher than those observed in the tissue plots (Figure 3.47 bottom). The much elevated **alkylated** dibenzothiophenes are unique to this sample as generally phenanthrene and dibenzothiophene concentrations are of similar magnitude.
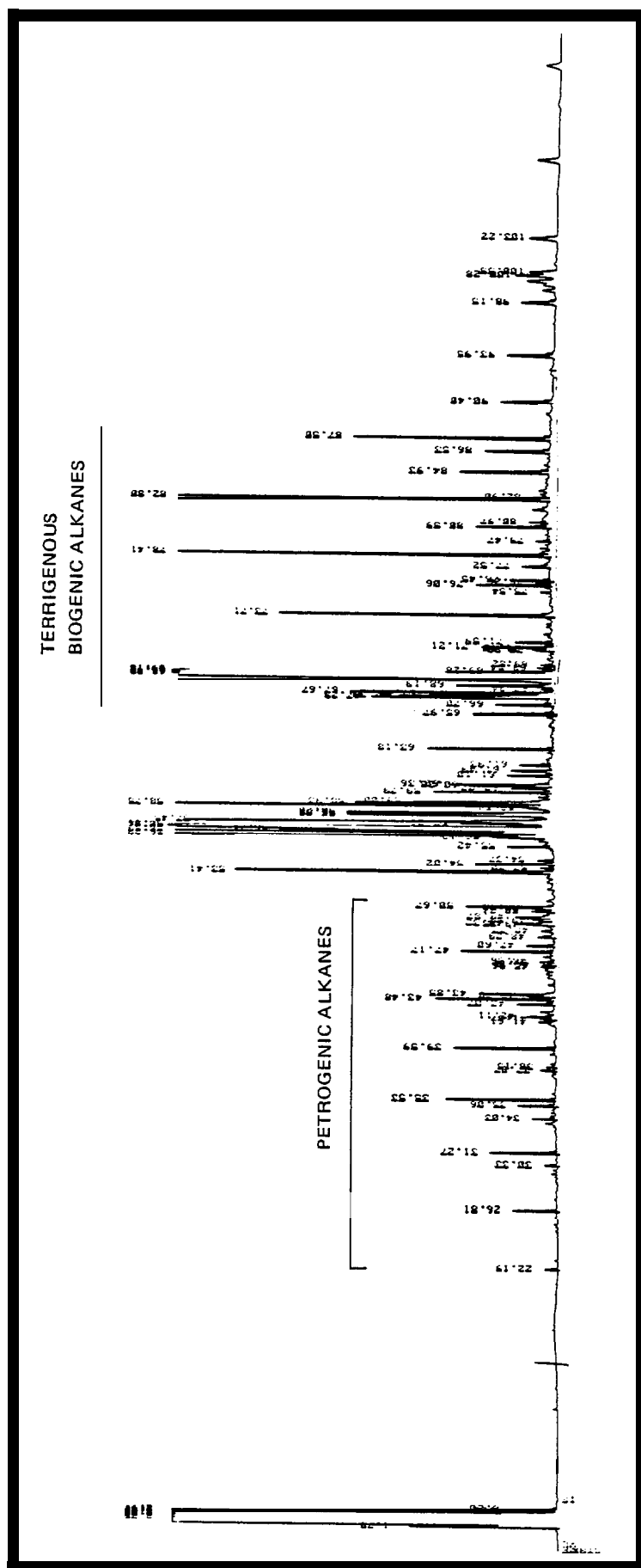
-184-

Figure 3.64. GC^2 Trace of Bay 11 Sediment Sample (Station H1; 9/12).
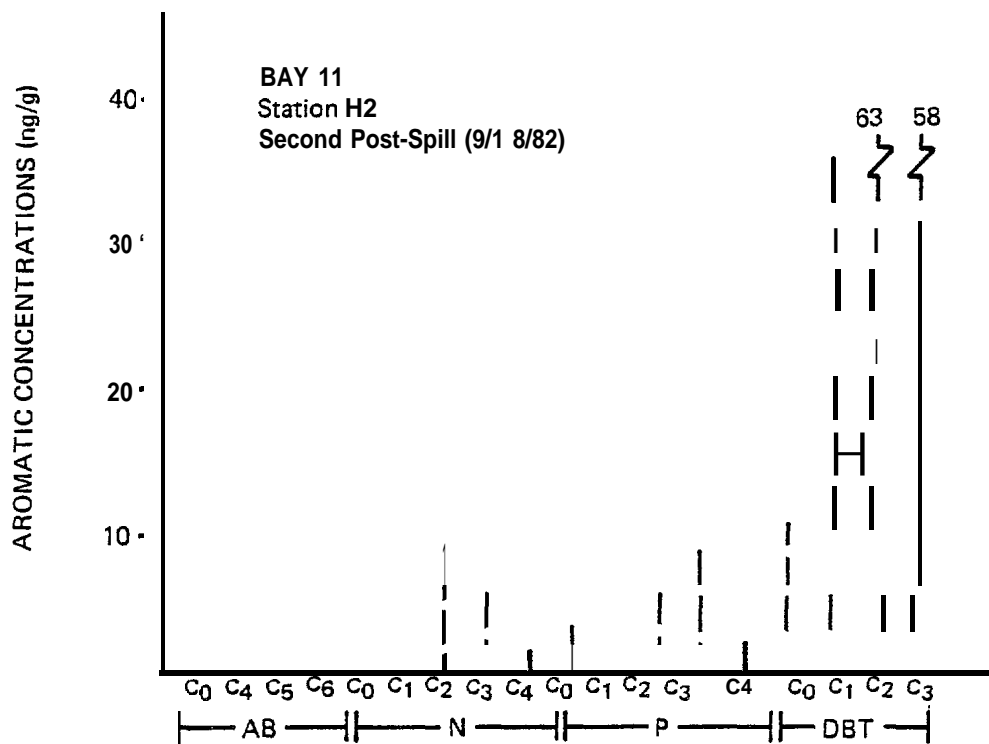
Figure 3.65. GC/MS Results from Bay 11 (H$_2$) Microbiology Plot Sediment Sample.

3.2.5 Comparison of Concentrations of Petroleum Measured by UV/Fluorescence and Gas Chromatography

Two analytical methodologies, UV/Fluorescence (UV/F) and fused silica gas chromatography/flame ionization detection (GC^2), were primarily employed to measure the concentrations of petroleum in bottom sediment samples. A large number of samples were initially analyzed by UV/F to determine the concentration of oil after which a subset of the samples was reextracted and analyzed by GC^2 to determine both the concentration and composition of the oil. The UV/F technique is sensitive to fluorescent aromatic compounds and is insensitive to non-fluorescing compounds such as saturated hydrocarbons. The GC^2 technique measures both saturated and aromatic hydrocarbons with approximately equal sensitivity.

A comparison of the UV/F and GC^2 measurements in sediments was complicated by the background signals from naturally occurring compounds. Biogenic saturated hydrocarbons such as $n-C_{27}$, $n-C_{29}$, $n-C_{17}$ and pristane which were measured by GC^2, were found not only in the spilled oil but also in uncontaminated marine sediments collected prior to any oil spillage.

Biogenic unsaturated compounds predominated in the aromatic fraction's gas chromatogram and obscured the measurement of aromatic hydrocarbon concentrations by GC2. Consequently, phytane which is a component of petroleum not commonly found in unpolluted marine sediments, was used as an indicator of the oil concentrations measured by GC^2.

A scatter plot of the concentration of oil measured by UV/F versus the concentration of phytane found in sediment

samples (Figure 3.66) shows the correspondence of UV/F and GC^2 measurements. The equivalence line is a plot of the concentration of phytane in the sediments expected from the UV/F concentration of oil. The slope of the line was determined from the concentration of phytane found in the original <u>Lagomedio</u> oil (6.4 milligrams/gram of oil). With the exception of six of the microbiology sediment samples, the correlation between the UV/F and GC^2 measurements follows the equivalence line.

Those six microbiology sediment samples were collected from stations H4, H5 and H6 in Bays 9 and 10 on August 30 and September 5. The deviation from the equivalence line suggests that these samples contain either relatively higher concentrations of phytane and other saturates (by GC^2) or lower concentrations of two and three-ringed aromatics (by UV/F) than the original oil, perhaps due to preferential loss of aromatics. This suggests that the petroleum in these sediments during the first week following the dispersed oil spill was chemically different from the original <u>Lagomedio</u> oil.

3.2.6 <u>Statistical Methodology for the Comparison of Sediment Data</u>

Concentrations of petroleum were measured in samples collected from five fixed sites (tissue plots) located along each of two depth strata in each experimental bay. During the 1981 field season, samples were collected from each of the four bays during three time intervals designated prespill, 1st postpill and 2nd postspill. (Details of sampling were described in Section 2.1). A total of 24 sample groups (4 bays x 3 times x 2 depth strata) each containing from two
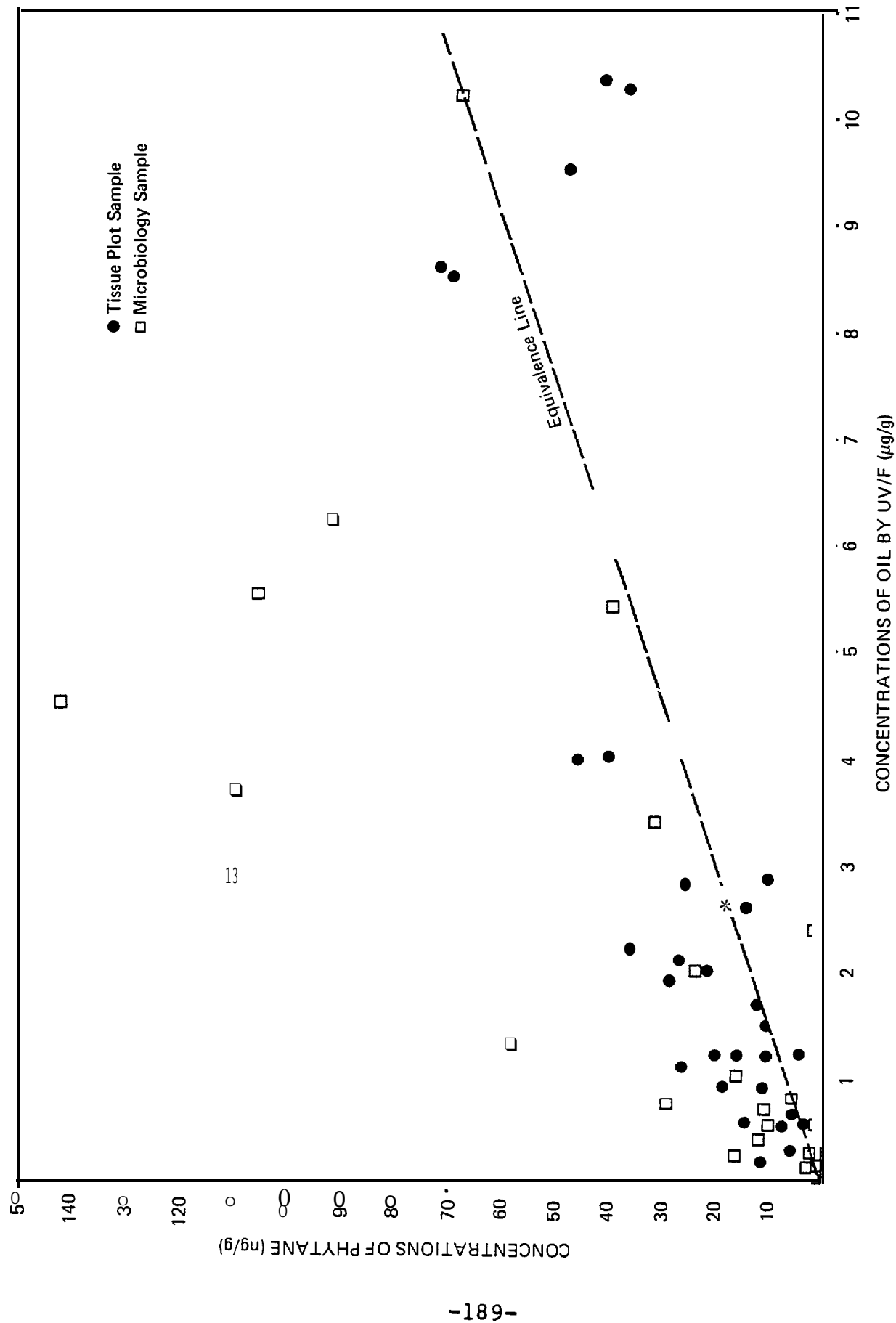
Figure 3.66. Comparison of concentrations of petroleum measured by UV/Fluorescence and Gas Chromatography.

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to five samples result for bottom sediment and surface floe
collected from the tissue plot sites.   Twelve additional
sediment samples collected during the 2nd postspill sampling
from fixed sites located along the two benthic biology
sampling lines in each bay were also analyzed.

The tissue plot data set was coded as concentration of
petroleum measured by UV/F in units of micrograms per gram
dry weight.   The data were treated according to methodologies
outlined in Green (1979).   The variances of the sample
groups were found to be heterogeneous using Bartlett's test.
Since a plot of LN S_i^2 vs LN Xi suggested a
dependence of the variance on the mean, the data were
transformed using the log transformation, $Z = \ell n$ (Xi +
1).   The transformation removed some but not all of the
heterogeneity of variance.   The square root transformation,
$z =$ SQRT (X_i), also failed to completely remove the
heterogeneity of variance.   Consequently, the log transformed
data were used in all statistical calculations.

The means and 95% confidence intervals for each data
group were calculated according to the following formula
from Sokal and Rohlf (1969 p. 145):

95% confidence interval $\bar{} \pm t_{.05} [n-1] S/ \sqrt{n.}$

Both the mean and the confidence interval were calculated
using the log transformed data and back-transformed to the
original units for presentation.   Statistical data are reported
using the following format: geometric mean (lower 95% confi-
dence limit, upper 95% confidence limit) or $X_G[,]$.
Summaries of the statistical data for sediments and floe from
tissue plot sites and for sediments from the benthic biology
sampling lines appear in Tables Al, A2 and A3 of Appendix A.

Sample groups were tested for a statistically significant
difference in means using the t-test (**Sokal** and **Rohlf,** 1969,
pp. 216-226). The appropriate comparison was made depending
on whether the two sample groups had equal *or* **unequal numbers
of observations.** The probability that the two sample group
means were indistinguishable was determined from the
t-distribution.

Summaries of the **intra-** and inter-bay comparisons for
surface sediments and floe appear in Tables A4 through A9 of
Appendix A. Discussions of the chemical significance of
these comparisons appear in previous "Results" sections.
This section summarizes the comparisons.

3.2.7 Oil in Beached Sediments

3.2.7.1 Bay 11 Beach

The concentration of oil and its composition along two
transects perpendicular to the beach face were examined by
GC^2 analysis. Samples were taken at the low-, mid-, and
high-tide marks along the two beach transects and samples
examined to determine (1) changing composition with time,
(2) changing concentrations of oil with time, and
(3) changing composition and concentration along with each
transect.

Results are summarized in Table 3.21. The concentra-
tions of oil in the beach sediments change at each sampling
location during the first month after the spill and subsequent
beaching of the oil. Variations in absolute concentrations
noted in Table 3.21 (e.g., Transect 4/HI) probably can be
ascribed to sampling variability because there seems no

TABLE 3-21

BAY 11 BEACHED OIL (GC^2 DATA)

BAY	TRANSECT/ LOCATION	DATE	SATURATES (f]) (mg/g) DRY WEIGHT BASIS	WET WEIGHT BASIS	AROMATICS (f$_2$) (mg/g) DRY wEIGHT BASIS	WET WEIGHT BASIS	TOTAL DRY WEIGHT BASIS	WET WEIGHT BASIS	WEATHERING PARAMETERS ALK/ISO	PRIS/PHY	SHWR
11	4/HI	8/20/81	120	40	63	21	180	61	2.64	0.83	2.51
11	4/MID	8/20/81	6.1	3.7	2.9	1.8	7.9	5.5	2.71	0.84	2.35
11	4/LOW	8/20/81	20	32	10	5.0	30	17	2.79	0.88	2.89
11	4/HI	9/15/81	0.36	0.24	0.11	0.07	0.47	0.31	1.83	0.86	1.18
11	4/MID	9/15/81	24	14	8.5	5.1	33	19	2.78	0.83	1.85
11	4/LOW	9/15/81	7.4	4.5	2.5	1.6	9.9	6.1	2.76	0.80	1.48
11	6/HI	8/20/81	54	18	27	9.1	81	27	2.72	0.81	2.81
11	6/MID	8/20/81	1.4	0.9	0.7	0.5	2.1	1.4	2.84	0.73	2.40
11	6 /LOW	8/20/81	9.4	6.2	4.5	3.0	14	9.2	2.71	0.82	2.51
11	6/HI	9/15/81	18	11	6.5	3.9	25	15	2.89	0.82	1.52
11	6/MID	9/)5/8)	17	5.9	6.0	2.1	13	8.0	2.67	0.87	1.61
11	6/LOW	9/15/81	15	5.1	5.5	1.9	21	7.0	2.72	0.82	1.78

likely mechanism for a decrease in oil concentration at the high-tide mark with no equal or greater decrease at the low- and mid-tide marks.

Although total oil concentrations remained in the 10-20 mg/g dry weight range during the one-month post spill period, the beached oil weathered moderately mainly due to evaporative losses of light saturates and aromatics. For the most part indications of biodegradation (ALK/ISO; Table 3.21) show no significant biodegradation. However at lower concentrations (i.e., Transect 4, HI; September 15) acceler- ated loss of n-alkanes relative to isoprenoids (ALK/ISO = 1.8) may be indicative of the onset of some microbially- mediated degradation. This sample has also suffered sub- stantial loss of light saturates (SHWR = 1.8) and aromatics (Figure 3.66 vs. 3.67) indicating that as oil concentrations decrease, weathering processes accelerate. The extent of evaporative loss from beached oil samples ranges from 40-67 percent in the September 15 samples (SHWR = 1.5-1.9). This indicates that from 40-67 percent of the evaporative losses possible for this oil have occurred during this period. (Note, this does not indicate a loss of 40-67 percent of the oil by weight.)

Loss of aromatics parallel the saturate losses. Loss of alkylated benzenes and naphthalenes proceeds mainly due to evaporation. After one month, most samples still contain significant C_2-C_4 naphthalenes, although the most extensively weathered sample (Transect 4, HI; September 15)is devoid of these naphthalenes (see Figures 3.67 and 3.68). That loss is due to evaporation rather than dissolution is suggested by the similarity in the composition of the Transect 6 samples, the low-tide sample being flushed to a greater
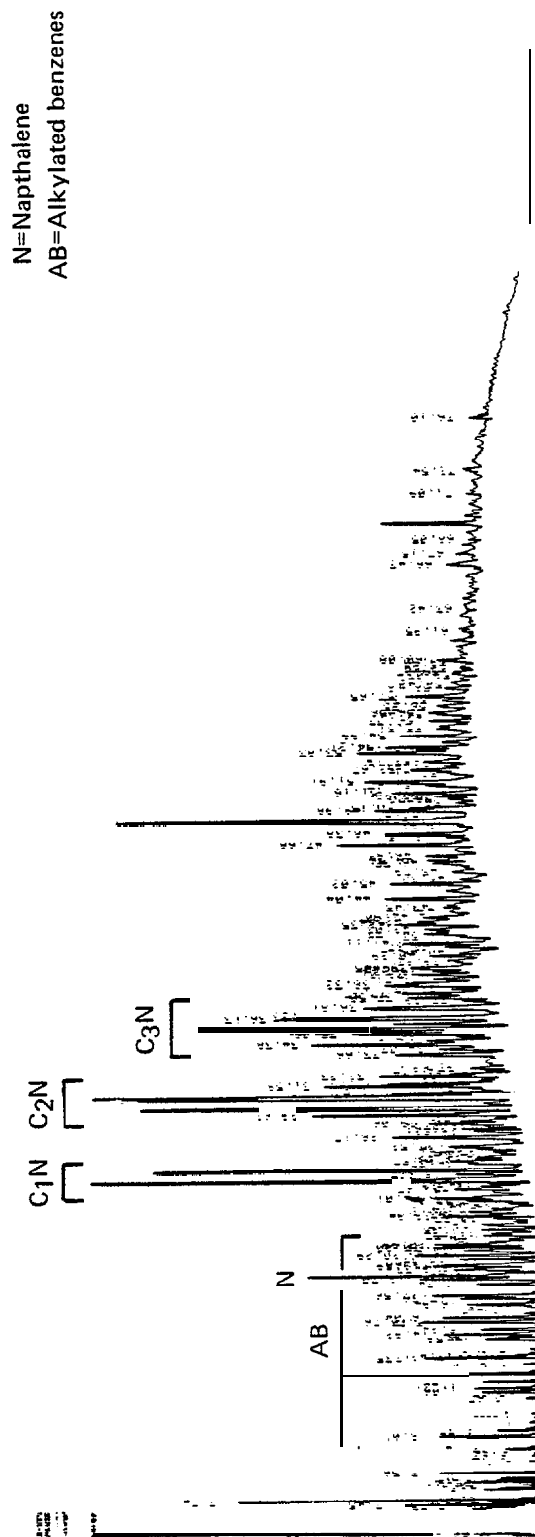
Saturates (SHWR=2.4)

10 11 12 13 14 15 16 17 18 19 20

Aromatics

N=Napthalene
AB=Alkylated benzenes

C₁N C₂N

C_1N C_2N

C_3N

N

AB
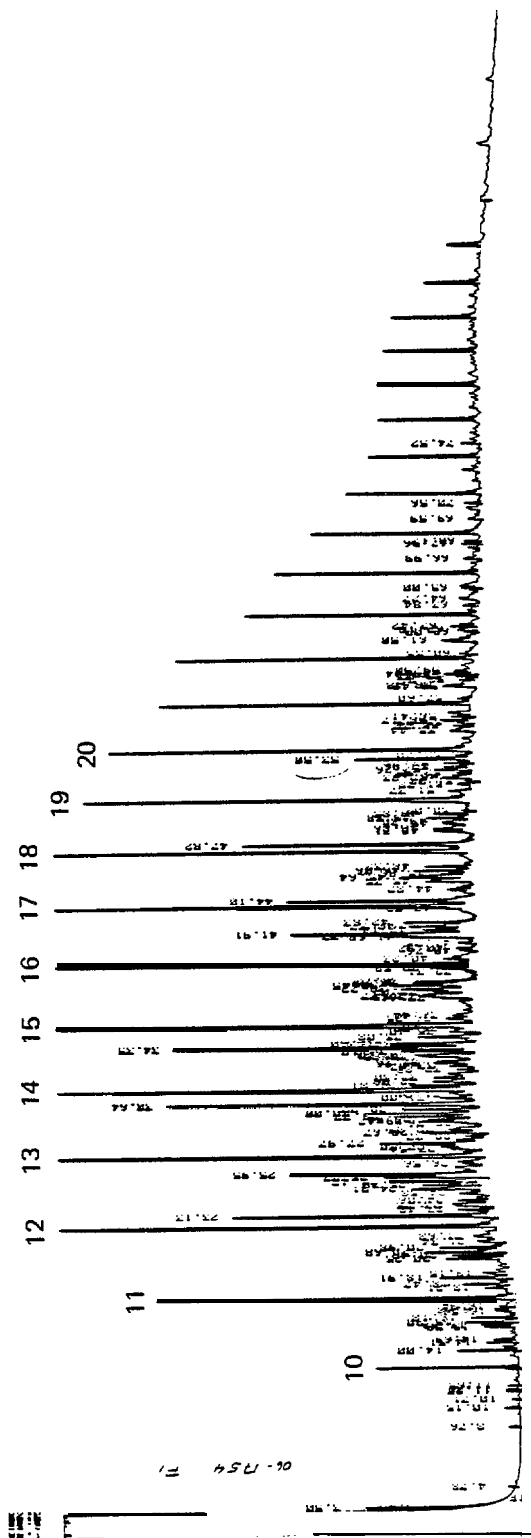
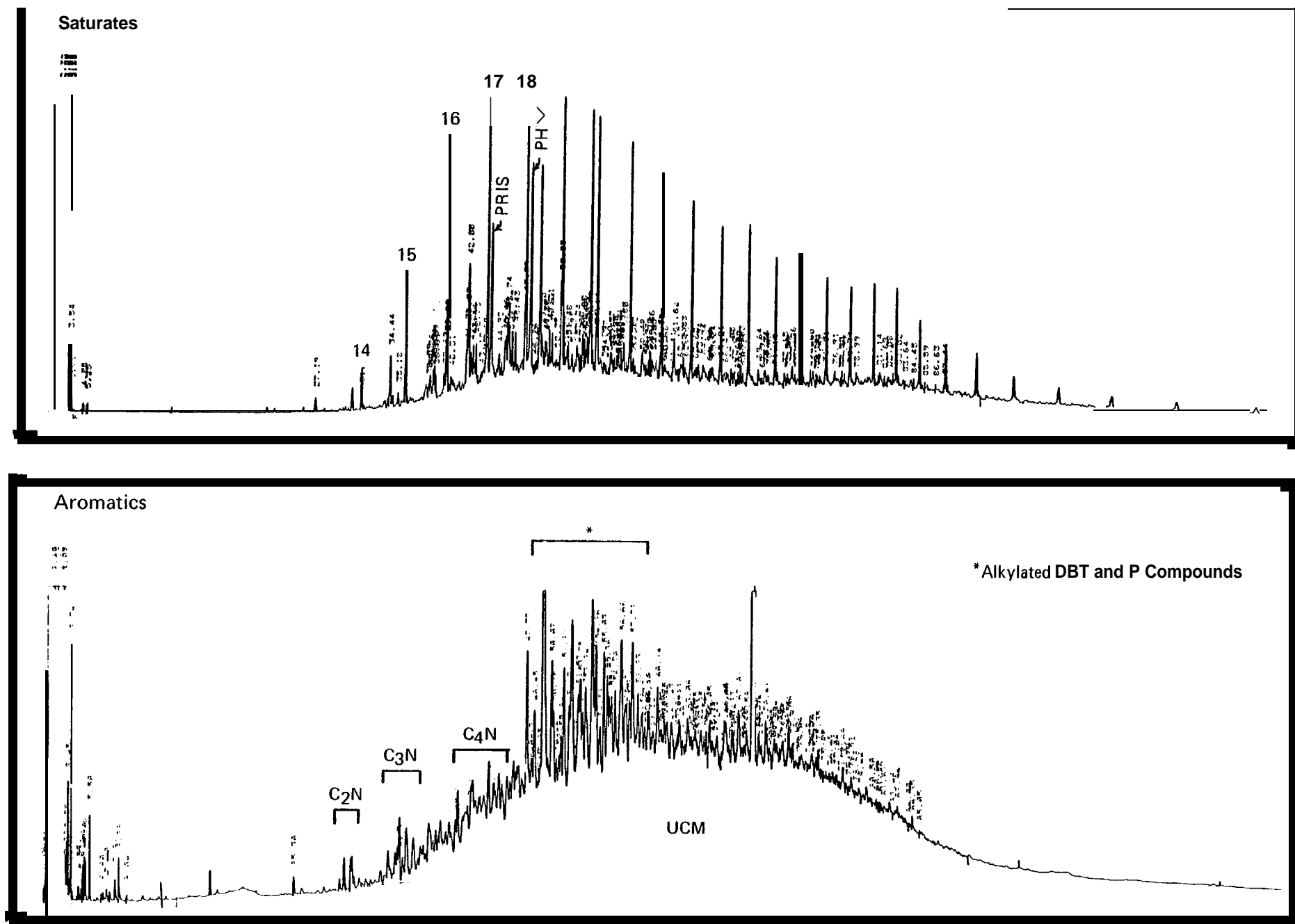Figure 3.67. GC^2 profiles of beached oil from Bay 1   after one day's stranding.

Figure 3.68. GC^2 profiles of beached oil from Bay 11 after 1 month stranding.

extent by seawater and hence potentially subject to greater losses by dissolution (Figure 3.69).

The similarity in **pristane/phytane** ratios in all samples indicates that no external influences (**i.e.,** the additional **biogenic** material containing pristane) have obscured the weathering parameters.

3.2.8 Bay 9 Beach

Four samples of Bay 9 beach sediment were obtained to determine **if** detectable dispersed oil residues were observed on the beach. No observable oil was present at the time although a "vegetable **oil**"-looking film was apparently coating the sediment.

No oil was detected at the high tide (beach berm) line. Low levels, 5-10 ppm (Table 3-22), were observed at the mid and low points on the beach transect. Interestingly, this is roughly the same level observed in the **bottom sediments** from this bay. The oil was weathered, roughly to the same extent as was observed in the bottom sediment (**SHWR** = 1.5) and no biodegradation was noted. A large peak at approximately $n-C_{25}$ in the GC^2 **trace,** a **phthalate acid ester, was** observed. The presence of this peak may be attributed to an impurity in the dispersant and was noted in other GC^2 traces of low-level water samples.

Aromatics TR 6 High

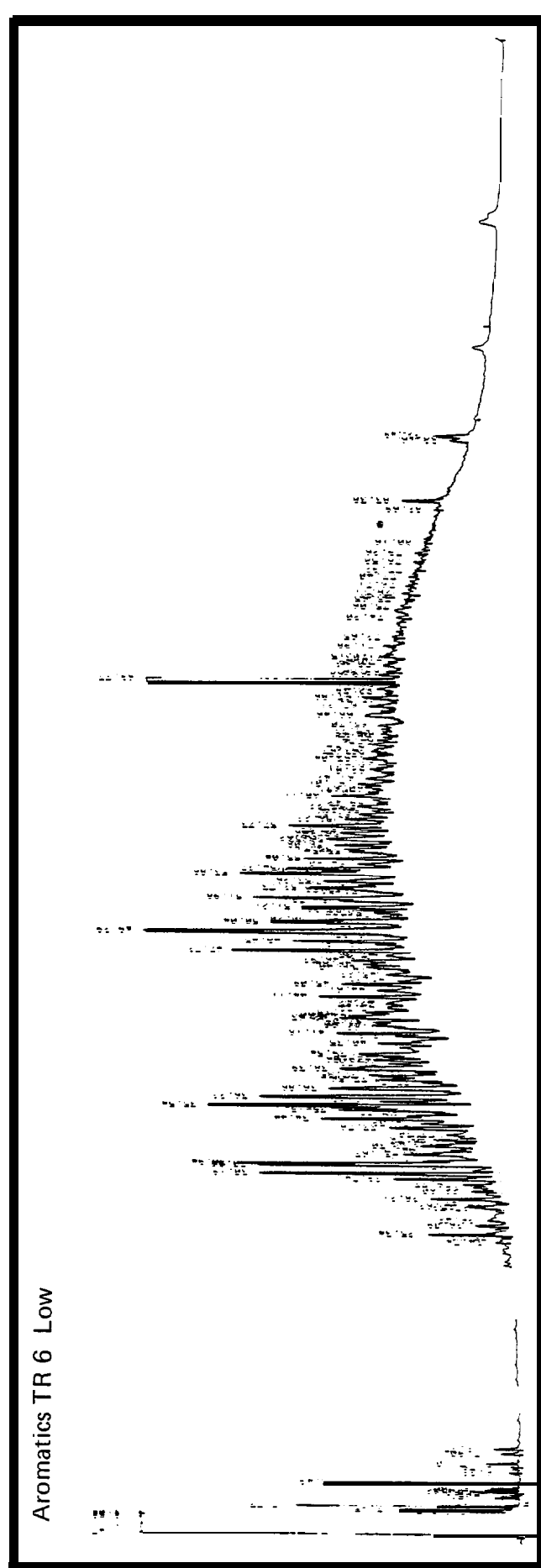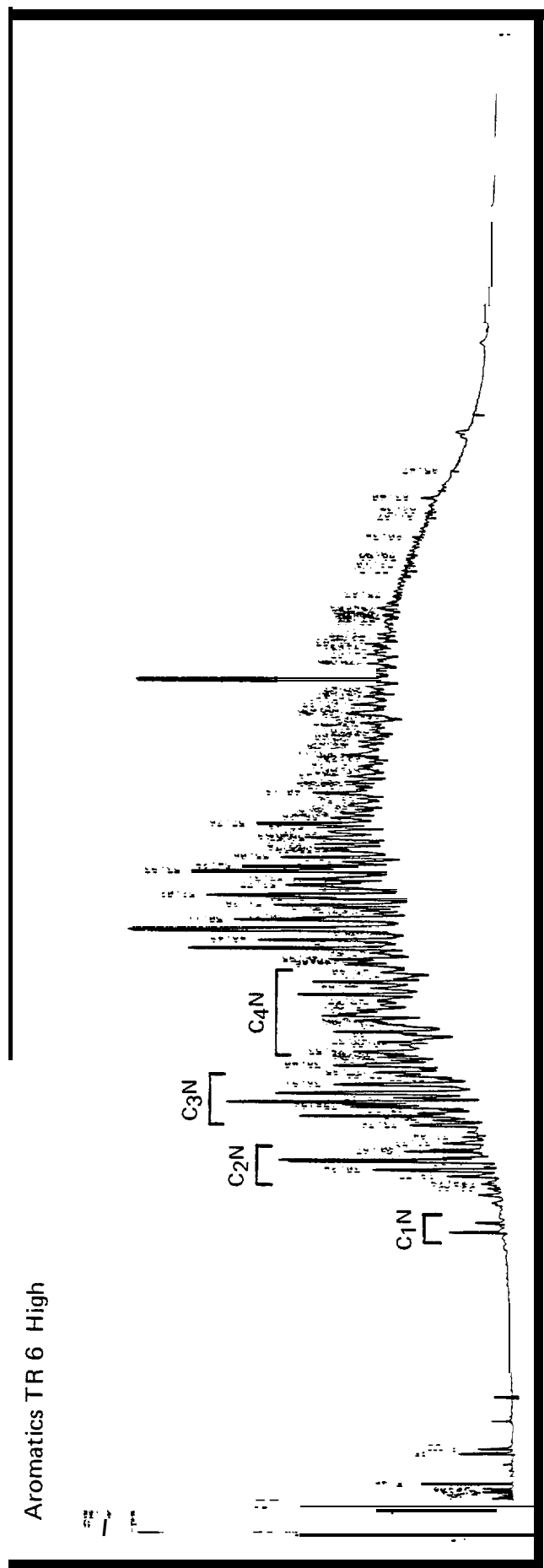Aromatics TR 6 Low

C1N

C2N

C3N

C4N

Figure 3.69. GC^2 profiles of beached oil, Bay 11, illustrating identical composition of aromatics from the upper and lower points in Beach Transect 6.

TABLE 3-22

BAY 9 BEACHED OIL (GC^2 DATA)

BAY	TRANSECT/ LOCATION	DATE	SATURATES (f_1) (119/9)	AROMATICS (f_2) ($\mu g/g$)	TOTAL ($\mu g/g$)	ALK/ ISO	PRIS/ PHY	SHWR
9	2/HI (surface)	8/31/81	.8	.5	1.3	-----no oil -----		
9	2/HI (subsurface)	8/31/81	.8	.6	1.4	-----no oil-----		
9	2/MID	8/31/81	5.3	2.1	7.4	--	1.3	1.4
9	2/LOW	8/31/81	3.2	1.4	4.6	--	2.5	1.5

3.3 Oil in Sediment Traps

A set of 23 sediment traps was analyzed by GC[2] to determine the quantity and composition of sedimented oil residues. The results of these analyses are presented here in Table 3-23.

In general, the sediment traps were deployed to fill the gap between the particulate oil in the water column and that in surface sediment/floc and benthic detrital feeders. Therefore, the quantitative capture of material was not essential. Indeed, there is no real way of firmly establishing a vertical flux rate from these trap data. The goals were to determine if oil was sedimenting in the various bays and to determine its composition.

3.3.1 Bay 9

Significant quantities of oil were trapped in Bay 9 during the O-3 day (post-spill) deployment. One cannot unequivocally determine the time or the rate of capture of this oil. What can be said is that the oil trapped in Bay 9 actively sank into the trap and that the oil's composition was that of a moderately to substantially weathered oil (SHWR=1.1-1.9). In the traps containing the most material (Table 3-23) though, the bulk of the hydrocarbons captured were saturated hydrocarbons (i.e. , individual n-alkane levels, $C_{12}-C_{30}$, 1-2 µg/trap). Light aromatics (C_1, C2, C3 naphthalenes) were captured to a small extent (20-70 ng individual component per trap $\simeq$ 0.5 µg total naphthalenes per trap; see Figures 3-70 and 3-71). After the initial (O-3 day) period, significant quantities of saturated hydro- carbons of a petroleum origin were observed in the 4-7 day

TABLE 3-23

SEDIMENT TRAP CONCENTRATION/COMPOSITION SUMMARY

BAY	TIME (POST-SPILL) (days)	STATION	DEPTH (m)	TOTAL EXTRACTABLE MATERIAL (µg/trap)	SATURATED HYDROCARBON FRACTION[a] (µg/trap)	AROMATIC HYDROCARBON FRACTION (µg/trap)	TOTAL HYDRO-CARBONS (µg/trap)	ALK/ISO[b]	SHWR[c]	AWR[d]
10	pre-spill		10	400	<5	<5	<5	--	--	--
	o-3	1	7	380	150	20	170	2.4	1.3	--
	0-3	6	3	300	30	5	35	1.6	1.6	--
	4-7	6	3	530	40	<5	40	--	1.2	--
	4-7	1	7	160	30	<5	30	0.8	1.3	--
	8-14	6	3	520	<5	<5	<5	--	1.0	--
	8-14	1	7	770	20	<5	~20	--	1.1	--
9	pre-spill		10	350	<5	<5	<5	--	--	
	o-3	1	7	190	60	10	70	2.0	1.1	--
	0-3	5	7	1320	130	20	150	1.7	1.9	--
	0-3	10	3	1000	280	30	310	2.4	1.4	NAD
	4-7	10	3	1770	50	<5	50	0.9	1.2	--
	4-7	5	7	550	90	<5	90	1.0	1.1	--
	4-7	6	3	80	<5	<5	<5	- -	--	--
	8-14	6	3	700	<5	<5	<5	--	1.1	-·
	8-14	1	7	580	80	<5	~80	0.4	1.0	-·
7	0-7	6	3	410	40	5	45	0.8	1.1	NAD
	0-7	1	7	400	30	5	35	1.1	1.5	--
	8-14	1	7	590	<5	<5	<5	- -	1.0	--
11	0-3	8	3	190	20	5	25	1.8	1.1	--
	0-3	8	3	180	10	5	15	1.8	1.1	--
	4-7	BQ	3	340	20	5	25	1.5	1.4	--
	4-7	BQ	3	240	30	5	35	1.9	1.2	--

[a]Corrected for biogenic input.

[b]ALK/ISO=2.5 $\overline{m}$ spilled oil.

[c]SHWR=2.5 in spilled oil.

'by GC^2/MS

NAD = no aromatics detected.
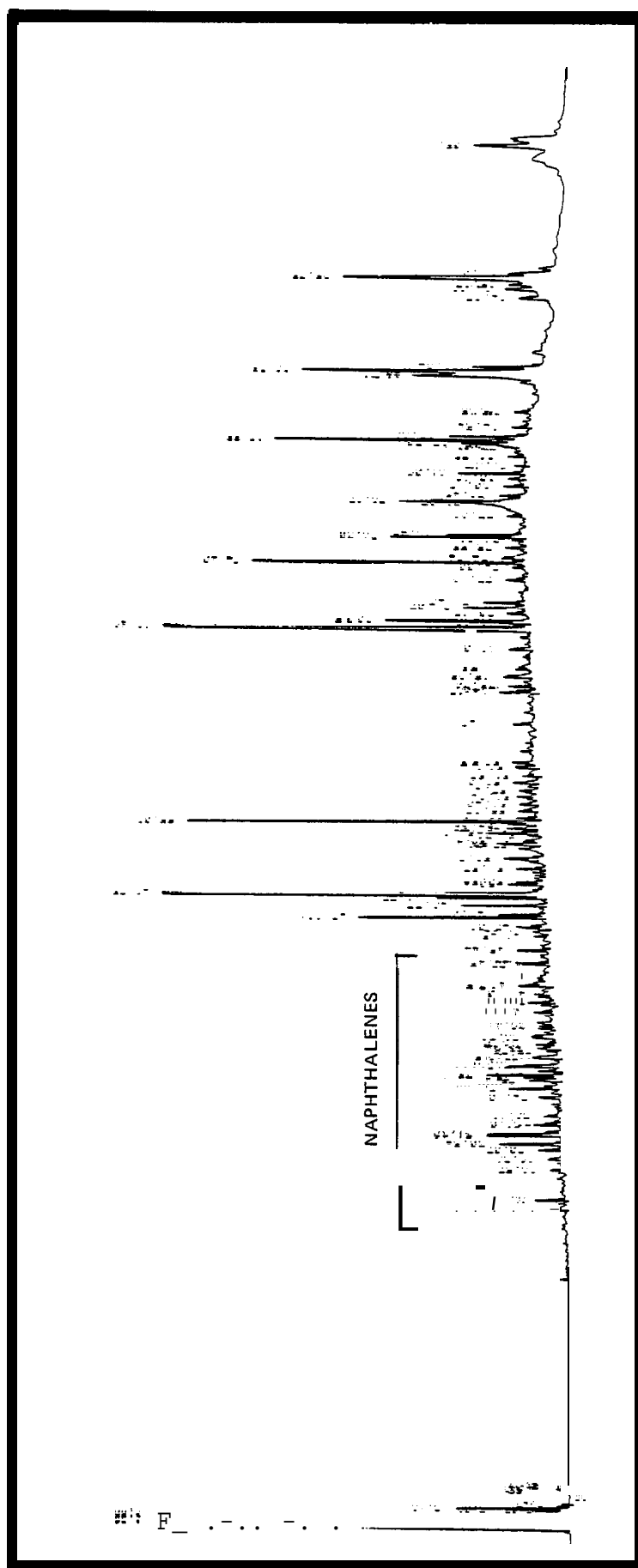
Figure 3.70. GC² Trace of Aromatic Hydrocarboons from Sediment Trap—Bay 9.

NAPHTHALENES

Bay 9 Saturates (0—3 Days)

12

17

Bay 9 Aromatics (O-3 Days)

Alkylated DBT and P

Bay 7 Saturates (O–7 Days)

Is

Figure 3.71. GC^2 Traces of Selected Sediment Trap Samples.

traps.   These residues were well weathered.   The decrease in
the ALK/ISO ratio (Table 3-23) is mainly attributable to
biogenic inputs rather than to biodegradation.   After the
0-3 day sampling, aromatic hydrocarbons were no longer
detected in the traps.   Indeed, GC^2/MS results from the
two samples examined failed to detect any aromatic
hydrocarbons.

One can make the rough calculation of an oil sedi-
mentation rate based on several assumptions: (1) Oil was
sedimented during the 0-1 day post-spill period, i.e. , any
subsequent capture is of resuspended bottom sediment floe
during sampling operations.   (2) The traps were efficient
collectors.   (3) No degradation of oil occurred in the traps.
(4) No dissolution of trapped particulate occurs, thus decreas-
ing observed concentrations.   We do not believe that a large
amount resuspension and capture are much of a problem due to
the absence of an odd/even straight-chain alkane preference
which would reflect resuspended terrigenous n-alkanes introduced
into the samples.   If ∿100-300 µg per trap are captured during
the first 24 hours, the traps having a cross-sectional area of
∿95 cm2, then the "pseudo-sedimentation rate" of oil could be
calculated as 1-3 $µg/cm^2$/day or 10-30 mg/m^2/day.   That this
number is similar in magnitude to that obtained in the floe
samples (2-10 mg/m^2) at the one-day post-spill sampling is
striking.   For all intents and purposes these numbers are the
same, given uncertainties in collection efficiencies of both
sediment trap and floe samplers.

Sporadic occurrences of petroleum in the suspended
particulate or resuspended particulate system are evidenced
by the incidence of captured weathered saturates of petroleum
origin in the 8-14 day trap deployments.

3.3.2 Bay 10

The 0-3 day results reported in Table 3-23 for Bay 10
traps indicate trapped oil concentrations in the 35-170
µg/trap range.   These oil residues are moderately weathered
(SHWR= 1.3-1.6) and minimally biodegraded (ALK/ISO=1.6-2.4).
Again, saturates are more abundant than aromatics with
aromatics representing 10-15 percent of the total hydrocarbons
captured as compared to a 33 percent share for the aromatics
in the hydrocarbon portion of the total oil (i.e., polars
not included).   A similar sedimentation rate calculation
yields a range of values of 4-20 $mg/m^2/day$ compared to a
known floe concentration of 2-7 mg/m^2.

Subsequent samples (4-7; 8-14 days) indicated very low
levels of well weathered saturated petroleum hydrocarbons
with no detectable aromatics present.

3.3.3 Bay 7

Very small quantities (35-45 µg/trap) of moderately to
highly weathered oil were captured in Bay 7 traps.   Here we
are approaching a background value of ~10 µg of hydrocarbons
(non-petrogenic) per trap.   The increased evidence of bio-
degradation (ALK/ISO=0.8-1.1) reflects the longer residence
time of this material in the system and its lower concentra-
tion, thus allowing for favorable biodegration kinetics.   Note
that apparently this very small level of sedimenting petroleum
in Bay 7 is non-detectable by both UV/F and GC[2] analyses of
surface floe and bulk sediment from this bay.

3.3.4 Bay 11

Like Bay 7, Bay 11 traps showed only very small quantities of mainly saturated hydrocarbon oil residues. These residues are highly weathered (SHWR=1.1-1.4) but virtually free of biodegradation influence. Though there is detectable oil in the samples, their levels are close to the detection limit of ~10 µg/trap, as are the Bay 7 samples, so these results must only be evaluated qualitatively.

3.4 Oil in Marine Organisms

3.4.1 Mya truncata

UV/F analyses to determine oil concentrations were performed on a total of 95 samples, comprised of 5 individual tissue plot stations on each stratum sampled (two strata from Bays 9, 10; one strata from Bays 7, 11) for three time periods (pre-spill; first and second post-spill). Additionally 5 individual Mya were analyzed from one tissue plot station to determine within-station variability.

GC^2 analyses were performed on pooled extracts from five tissue plot stations along each stratum during each time period. Additionally, the 5 individual Mya animals were analyzed as well as 3 individual tissue plot stations along one stratum. A total of 26 analyses were performed.

GC^2/MS analyses were performed on the stratum poolings plus 2 of the individual tissue plot stations (total of 21 analyses).

Additionally, normal quality control activities included the analyses of several analytical triplicates (i.e.,

3 subsamples of a single homogenate at a given station, refer to Section 2.2.9). All data for tissues is reported as the geometric mean ± the 95% confidence interval, on a dry weight basis (see also Section 3.4.7).

3.4.1.1 Bav 9

3.4.1.1a Oil Concentrations by UV/F

Oil concentrations determined by UV/F spectra of Mya tissues (Figures 3.72 and 3.73) were measured at a well defined *emission* maximum at 347-350 nm, by comparison with a daily standard curve of the Lagomedio oil. Two separate calibration curves were used for tissue data - one for high and one for low concentrations of oil. The UV/F spectra shown in Figure 3.74 illustrate typical spectra not only for the oil and for Mya, but for all other animals as well.

Pre-spill UV/F data for Mya contain 0.35 (.22, .49) ug/g dry weight of oil equivalents in the 7m stratum (Tissue plot stations 1-5), and 0.40 (.25, .56) in the 3m stratum (Stations 6-10). (Note, however, that pre-spill UV\F measurements reflect background fluorescence at 350 nm due to an unknown source. No oil was found (by GC[2]) in any pre-spill tissues samples of Mya or other species.) One day post-spill (28 August 1981) clams contained 121 (51, 290) ug/g of oil in the 7m stratum, and 215 (130, 350) ug/g in the 3m stratum. Mya oil concentrations during the second post-spill sampling (10 September 1981) were lower: 114 (90, 140) ug/g, 7m stratum, and 135 (120, 1S0) ug/g, 3m stratum. No statistical difference was found between data from 7m and 3m strata for any sampling period, or between data from the first and second post spill samples collected from the 7m stratum (Table 3-24, Appendix A).
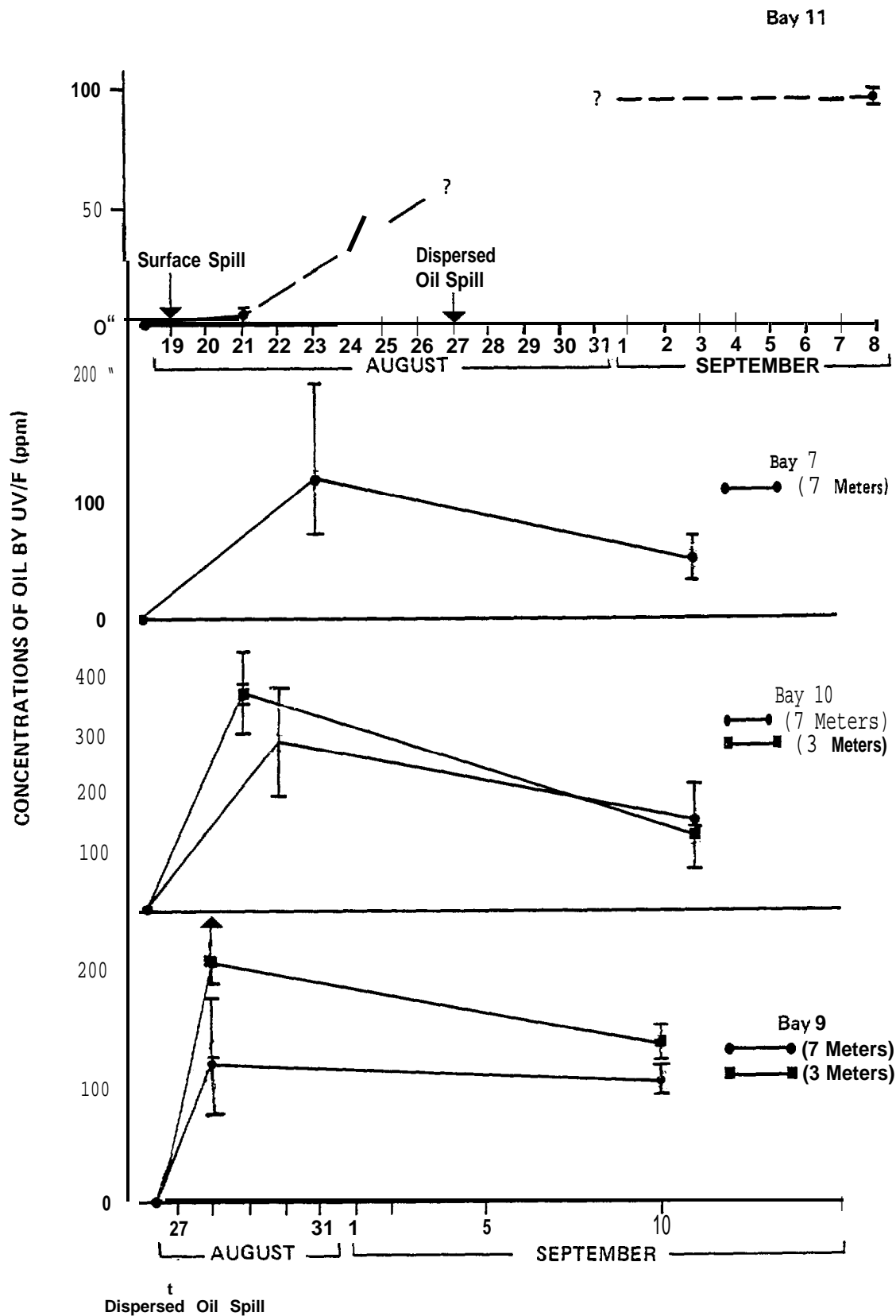
Figure 3.72. **Mya** truncata **Concentration Summary.**

PRESPILL
7-9 AUG 81

.23	.50	.33	.50	.45	3m
6	7	8	9	10	

.40 (.25, ,56)*

.37	.44	.31	.19	.44	7m
1	2	3	4	5	

.35 (.22, ,49)

FIRST POSTSPILL
28 AUG 81

194.	230.	350.	118.	251.	3m
6	7	8	9	10	

215.(130, 350)

211.	195.	43.	81.	183.	7m
1	2	3	4	5	

121. (51, 290)

SECOND POSTSPILL
10 SEP 81

128.	153.	147.	119.	129.	3m
6	7	8	9	10	

135. (120, 150)

115.	104.	116.	90.	152.	7m
1	2	3	4	5	

114. (90, 140)

*95% Confidence Limits

Figure 3.73. Concentrations of Oil in Mya truncata, Bay 9 by UV/F (fig/g).
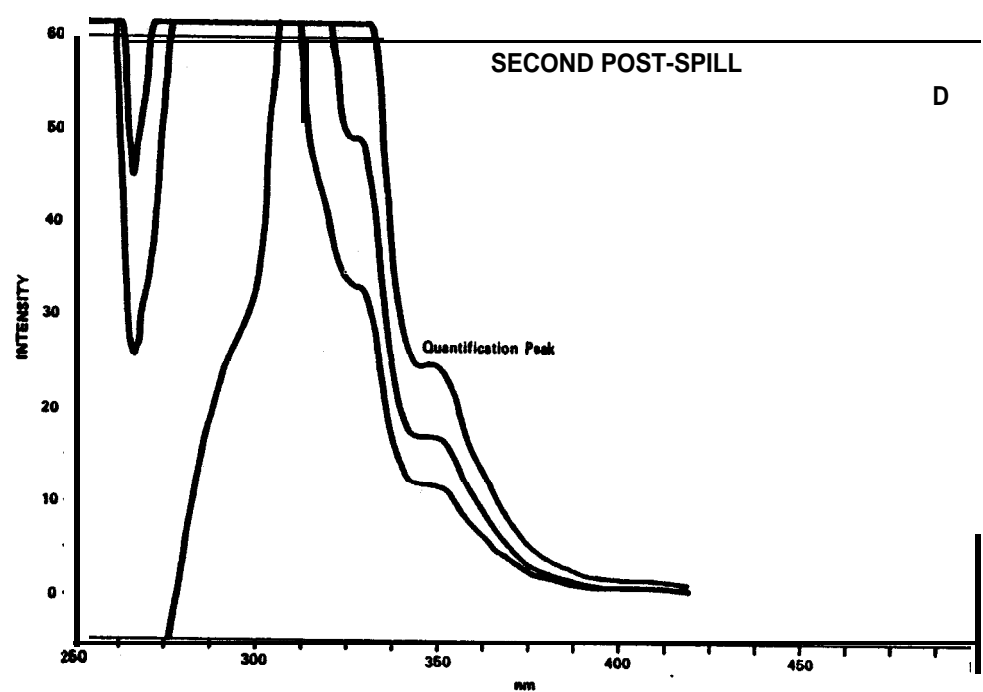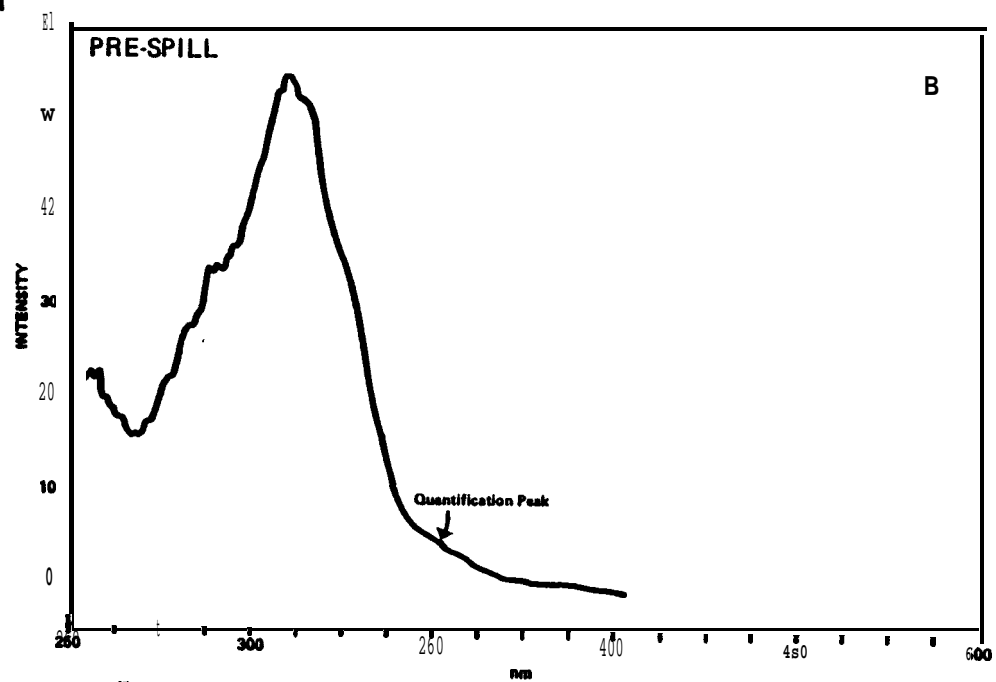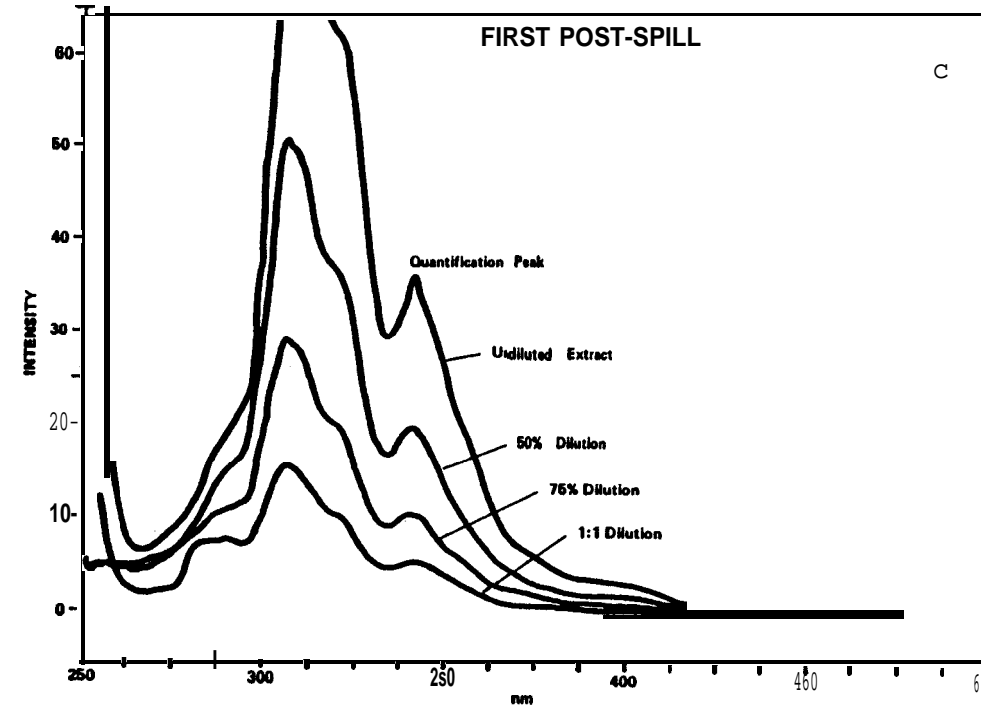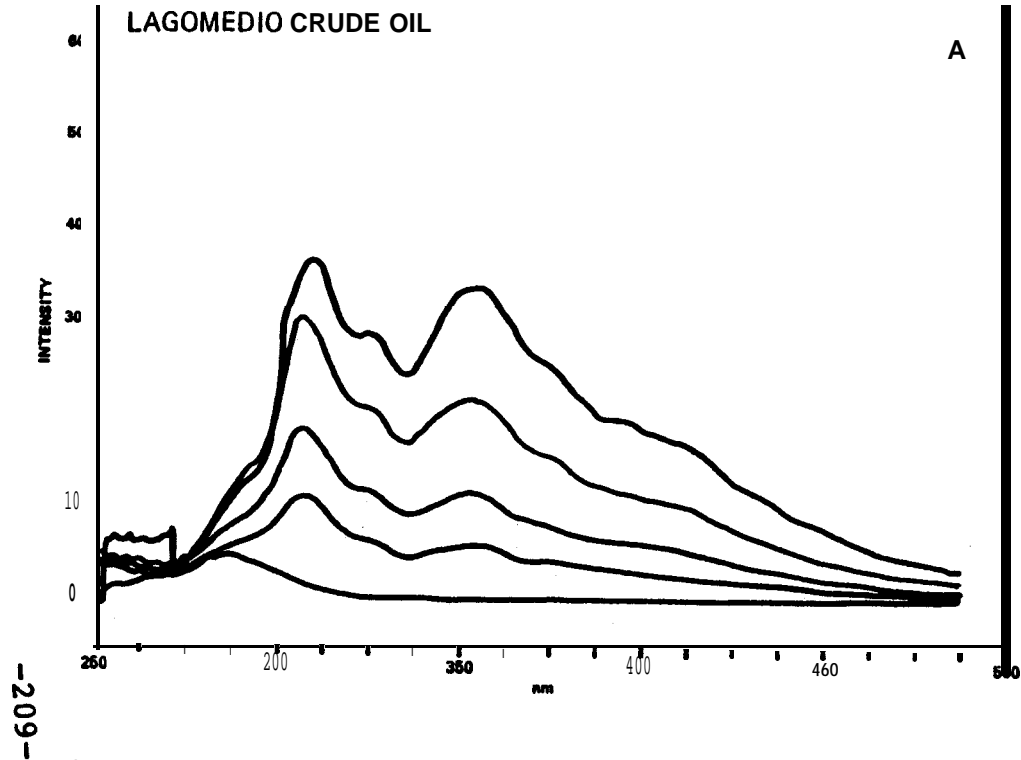
Figure 3.74. UV/F spectra of *Mya truncata* and of Lagomedio crude oil.

3.4.1.1b Oil Composition by GC[2]

The GC2 profile time series for the saturated (f_1) and aromatic (f2) hydrocarbons in **Mya** are shown in Figures 3-75 and 3-76.   **Pre-spill** samples contained only **biogenic** compounds. The one-day post-spill animals contain "fresh" oil with alkane components as low as $n\text{-}C_{10}$ observed in the tissues. Biodegradation proceeds rapidly within these tissues (Figure 3-75) with the **alkanes** being nearly totally degraded relative to the **isoprenoid alkanes** during the two-week **postspill** period.   This degradation is most likely due to bacterial activity within the animals themselves, rather than reflecting an assimilation of biodegraded residues. Indeed, there is no evidence for microbial degradation occurring to any significant extent in the water or sediment within this time period.

GC^2 profiles of the aromatics reveal the massive acquisition of "fresh" petroleum by **Mya** one day after the spill (Figure 3-76), followed by preferential loss of two ringed aromatics an increased relative importance of the **alkylated** phenanthrene and dibenzothiophene compounds, and a relative increase in the unresolved complex mixture **(UCM).**

3.4.1.1c Aromatic Hydrocarbon Composition by GC 2/MS

The changing detailed aromatic hydrocarbon profiles of **Mya** samples (analyzed by stratum) are shown in Figure 3-77. The profiles reveal that after an initial accumulation of **whole** "fresh" oil containing abundant naphthalene compounds as well as **phenanthrene, fluorene** (not shown), and **dibenzo-**thiophene compounds, extensive deputation of all aromatic
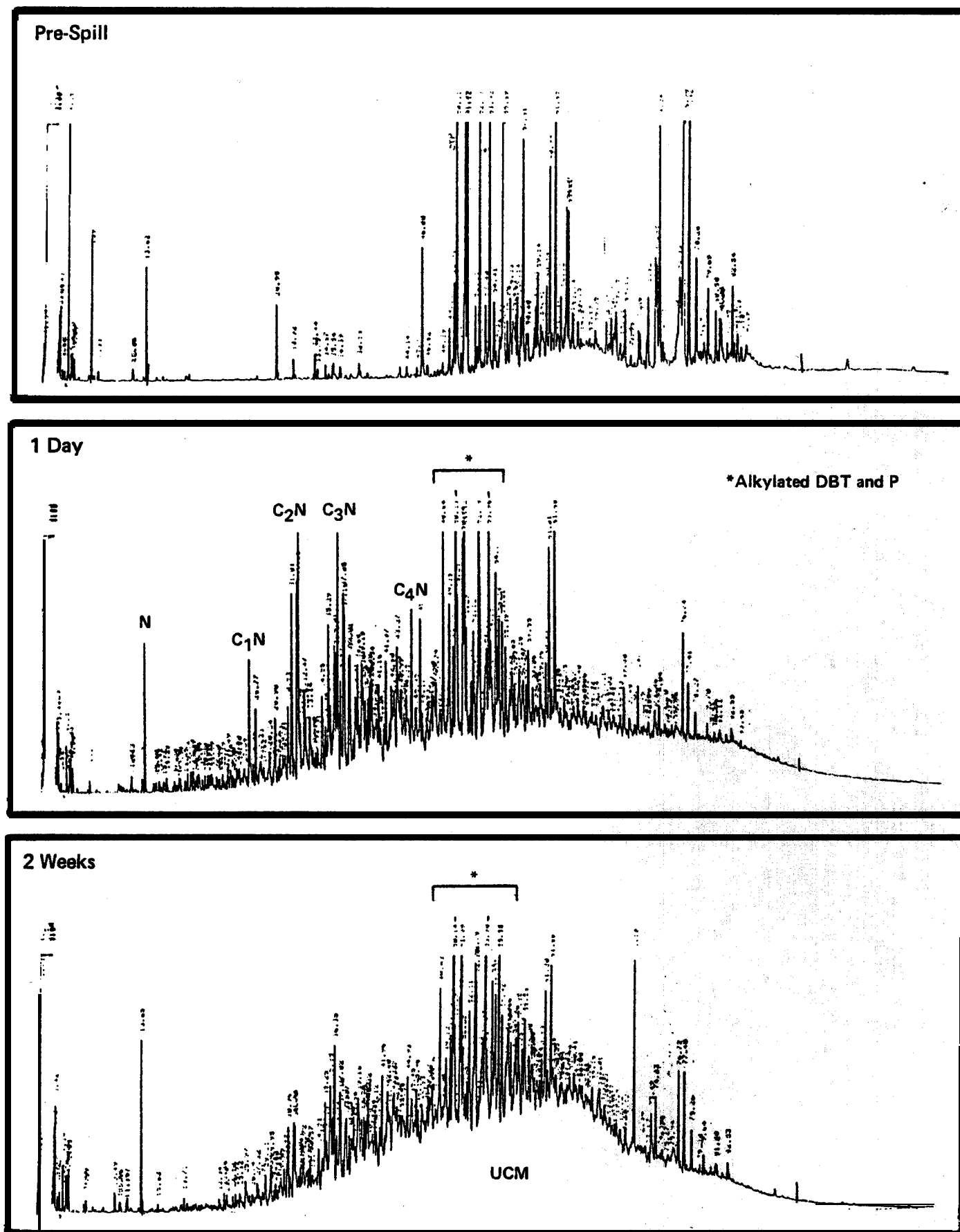
-210-

Figure 3.75. **MYA** truncata—GC^2 **Profiles of Bay** 9 **Animals (Saturated Hydrocarbons).**

Figure 3.76. **MYA truncata—GC^2 Profiles of Bay 9 Animals (Aromatics).**
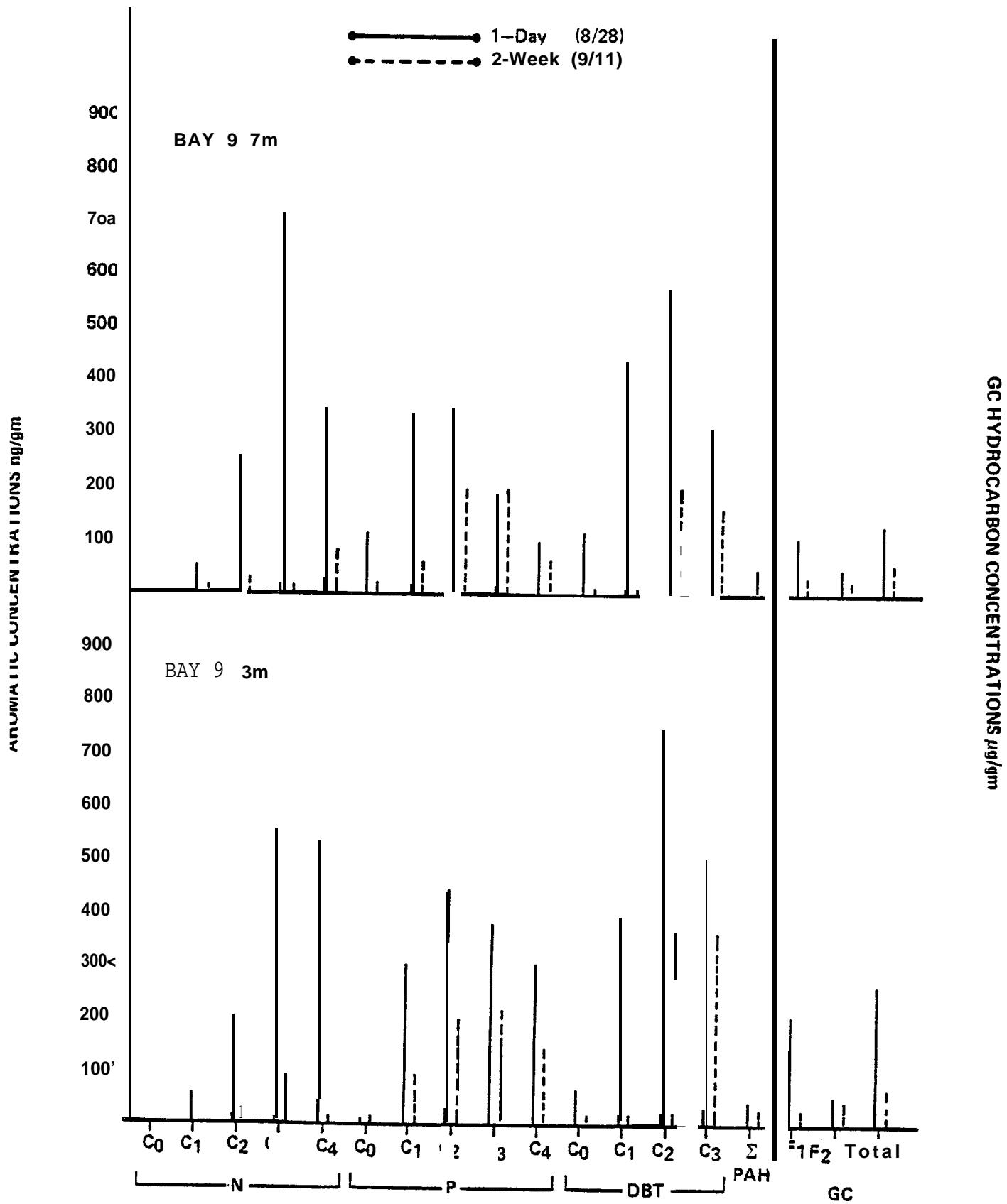
Figure 3.77. <u>MYA</u> Aromatic Profiles (by GC^2/MS).

compounds occurs. No **alkylated** benzenes were detected in any samples at either time interval. Note, however, that the relative degrees of deputation of two-ringed aromatics and the parent phenanthrene and dibenzothiophene are much greater than for the **alkylated** phenanthrene and dibenzothiophene compounds.

3.4.1.2 <u>Bay 10</u>

3.4.1.2a **Oil** Concentrations by UV/F

UV/F scans of tissue plot stations in Bay 10 revealed **prespill** concentrations of "oil equivalents" similar to those of Bay 9: 0.57 (.42, .74) μg/g, 7m stratum and 0.78 (.55, 1.0) μg/g, 3m stratum. The first post-spill samplings were undertaken on August 29, 1981 for Stations 6 to 10 and August 30, 1981 for Stations 1 to 5. First post-spill concentrations were high, at 277 (180, **420) μg/g,7mstratum,and** 368 (290, 460) μg/g, 3m stratum. As in Bay 9, the clams analyzed from the more shallow 3m stratum (Tissue plot stations 6-10) contained **higher** concentrations of oil. Bay 10 oil concentrations are roughly **twice** the concentrations found in Bay 9. Second post-spill clams (September 11) contained 157 (110, 230) μg/gm, 7m stratum and 131 (96, 178) μg/gm, 3m stratum, indicating a twofold reduction in total oil concentrations. This value is reasonably similar to September 11 concentrations in Bay 9, suggesting that, despite the higher initial post-spill oil concentration in Bay 10, the concentrations two weeks later may be a function of lipid storage capabilities and not the original concentration of oil. The first post spill concentrations may reflect oil levels in the animals' guts as opposed to assimilated oil stored in the clam **muscle. Furthermore, note** (Figure **3-72) that** the Bay 10 sampling

is 1-2 days after the Bay 9 sampling, perhaps indicating
continued oil uptake during the 1-3 day post-spill period.
Concentration data are summarized in Figures 3.72 and 3-78.

UV/F analytical replicates within Bay 10 are good. For
pre-spill data, triplicate samples from Station 3 averaged
0.67 ± 0.12 µg/g, and a second post-spill sample from Station 5
averaged 110.9 ± 3.3 µg/g (arithmetic means and standard
deviations).

3.4.1.2b Oil Composition by GC[2]

The GC2 profiles of Mya from Bay 10 revealed the
same compositional features as those for Bay 9 animals;
that is, rapid massive uptake of fresh oil followed by
deputation of both saturates and aromatics with preferential
loss of soluble aromatics and biodegradable n-alkanes.
The larger amount of oil initially acquired is of the same
composition nature (i.e., relatively unweathered oil) as
the Bay 9 animals.

3.4.1.2c Aromatic Hydrocarbon Composition GC[2]/MS

Detailed aromatic hydrocarbon results are presented in
Figure 3-79 for Bay 10 (7m stratum offshore and 3m stratum
nearshore) animals. Levels of aromatics are greater at the
inshore stratum than offshore, but aromatic profiles are
similar at both strata and echo trends observed in Bay 9.
That is, after rapid uptake of whole oil containing sizeable
quantities of toxic naphthalenes and other aromatics, nearly
all of the naphthalenes and C_0-C_1 phenanthrenes and diben-
zothiophenes are depurated leaving 40 to 60 percent of the

Figure 3.78. Concentrations of Oil in Mya truncata, Bay 10 by UV/F (μg/g).
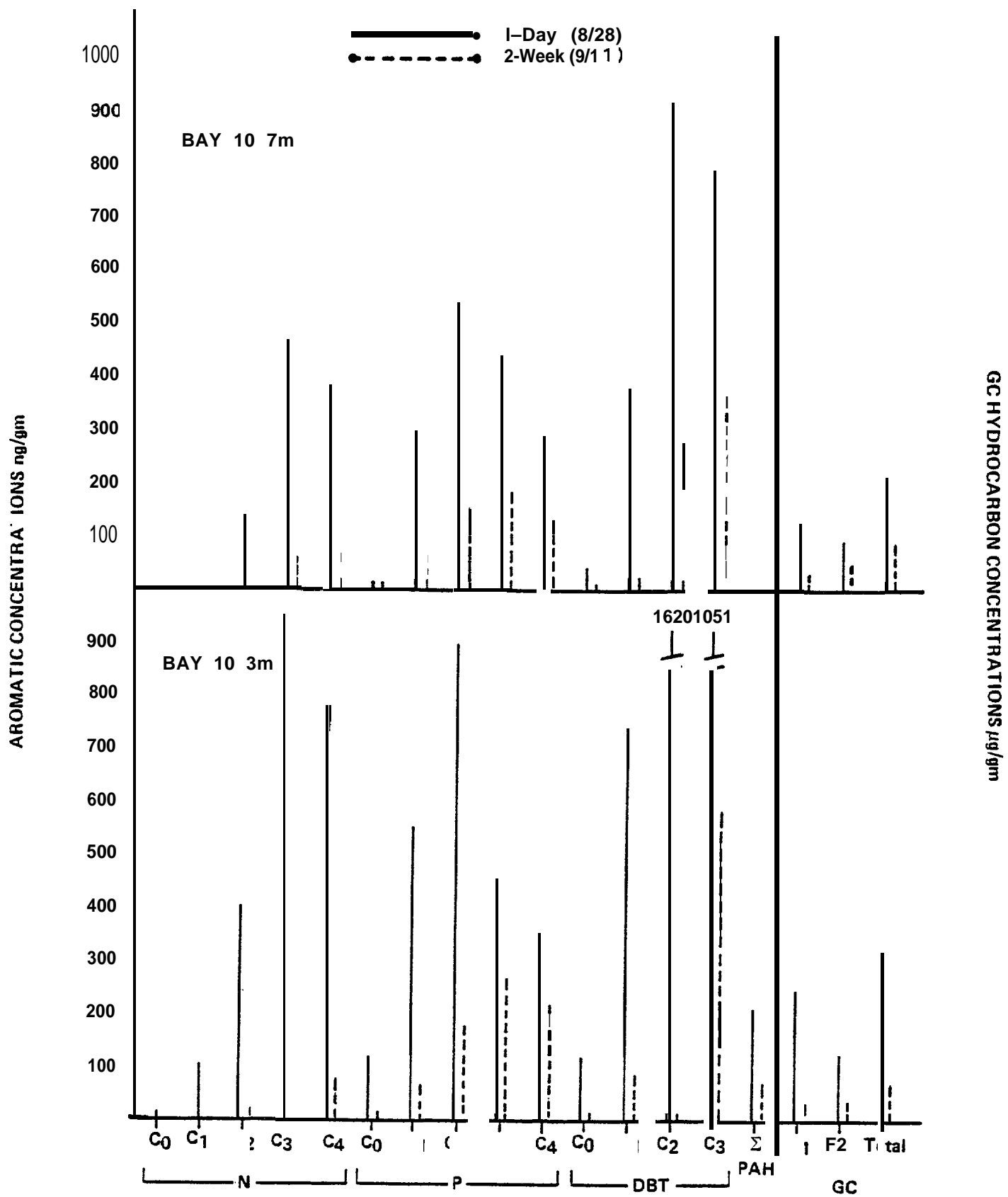
Figure 3.79. Aromatic Profiles from Mya Exposed to Oil, I Illustrating Changes in Concentrations Over 2 Weeks.

original amount **alkylated** phenanthrene and dibenzothiophene components (Figure 3-79). These findings indicate that the **alkylated** aromatics will continue to be the compounds of greatest interest in long-term tissue monitoring efforts.
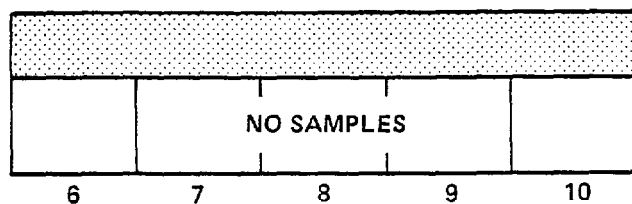

3.4.1.3 Bay 7

3.4.1.3a Oil Concentrations by UV/F

Oil concentrations by UV/F were at background levels (0.34 [.21, .48] µg/g, 7m stratum) for **pre-spill** clams in Bay 7. Levels rose to 114 **(64,** 210) µg/g for the first post-spill samples (August 31), and then dropped to 47 (31, 70) µg/g by the second post-spill sampling (September 11). (See Figures 3-72 and 3-80.)

3.4.1.3b Oil Composition by GC[2]

<u>Mya</u> from Bay 7 did acquire significant levels (up to ∼150 ppm) of petroleum. GC2 profiles (Figure 3-81) of the first one-day (August 31=3 days) animals reveals a hydrocarbon assemblage in the process of being degraded (i.e., intermediate between those observed in Figure 3-75 from Bay 9). Note the high abundance of pristane (natural and petrogenic) and high relative abundance (to $n-C_{18}$) of phytane **(petrogenic),** the latter indicating the biodegradation process. This process continues through the two-week sampling, in which the extensive biodegraded oil (albeit in lesser quantities than found at 3 days) is revealed (Figure 3.81). Aromatic profiles (Figure 3.82) reveal a significant three-day impact of aromatic petroleum residues as indicated by a large **UCM** and broad range of aromatic
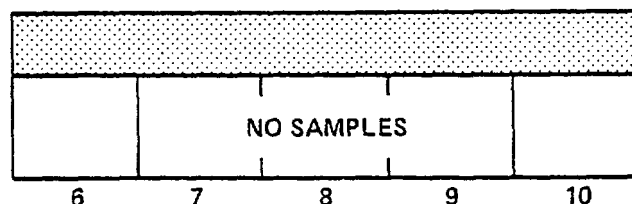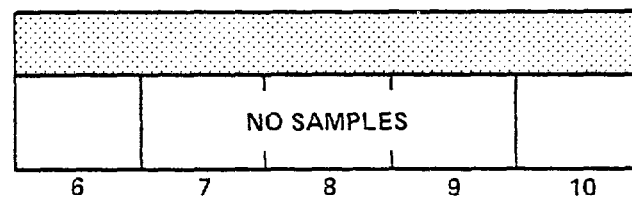
TISSUE PLOTS							PRESPILL 17 AUG 81

PRESPILL
17 AUG 81

3m — NO SAMPLES — 6 7 8 9 10

7m — .30 | .28 | .53 | .36 | .24 — 1 2 3 4 5 — .34 (.21, .48)*

FIRST POSTSPILL
31 AUG 81

3m — NO SAMPLES — 6 7 8 9 10

7m — 194. | 60. | 84. | 126. | 156. — 1 2 3 4 5 — 114. (64, 210)

SECOND POSTSPILL
11 SEP 81

3m — NO SAMPLES — 6 7 8 9 10

7m — 79. | 35. | 37. | 49. | 44. — 1 2 3 4 5 — 47. (31, 70)

*95% Confidence Limits

Figure 3.80. Concentrations of Oil in Mya truncata, Bay 7 UV/F(μg/g).
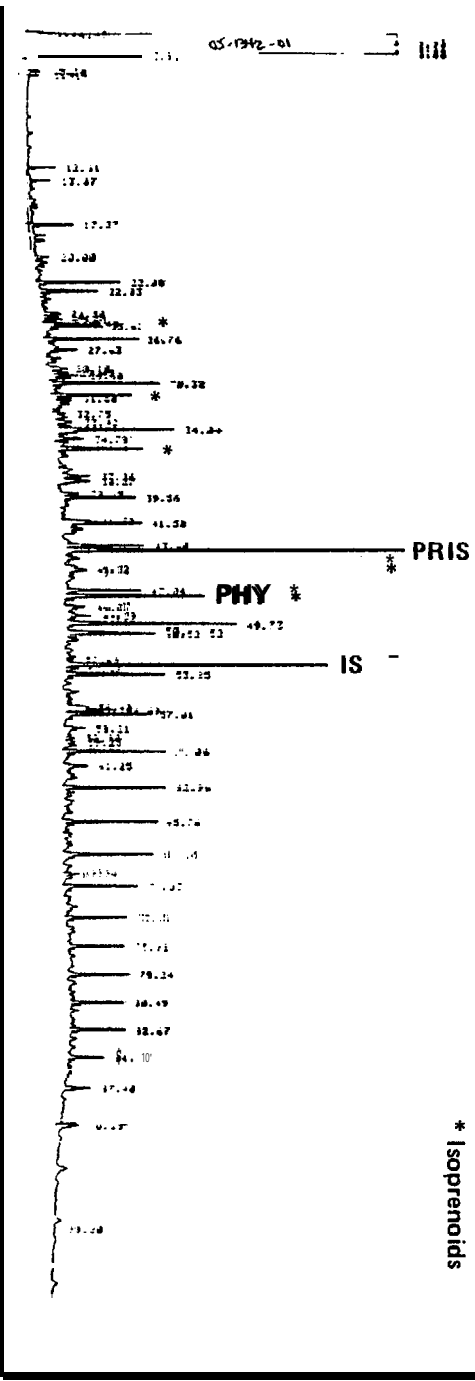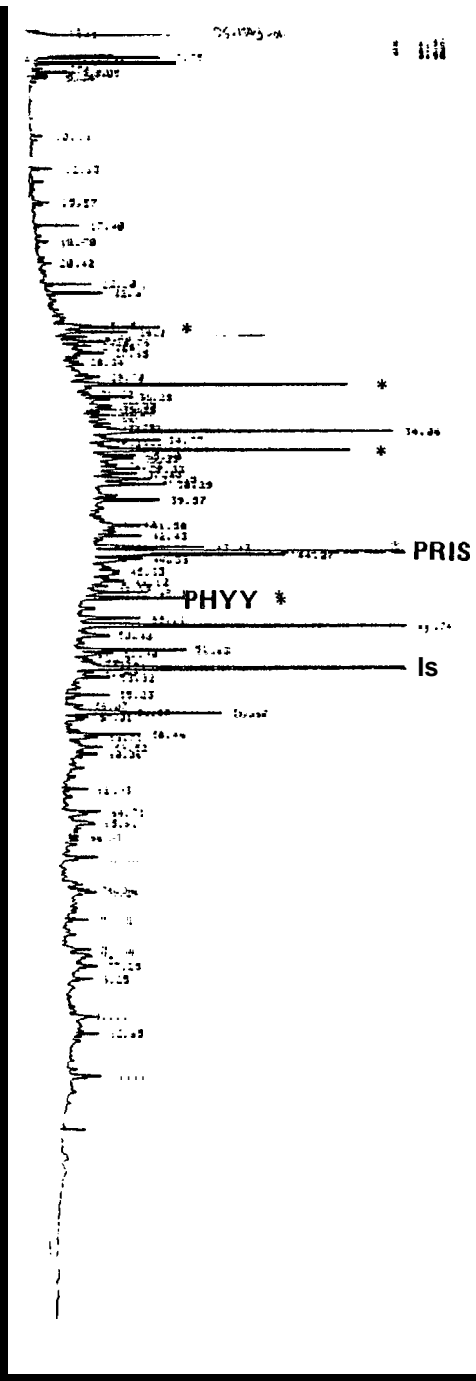
Figure 3.81. ___MYA truncata___—GC2 Profiles ○ Bay 7 Animals (Saturates)

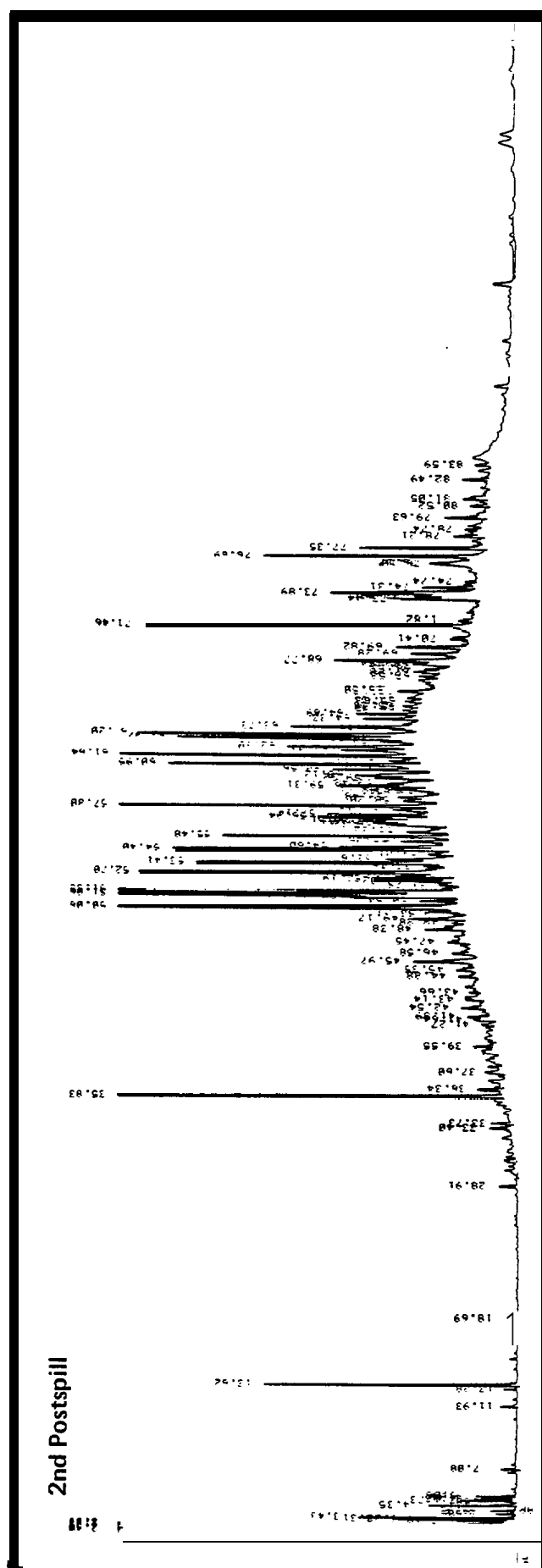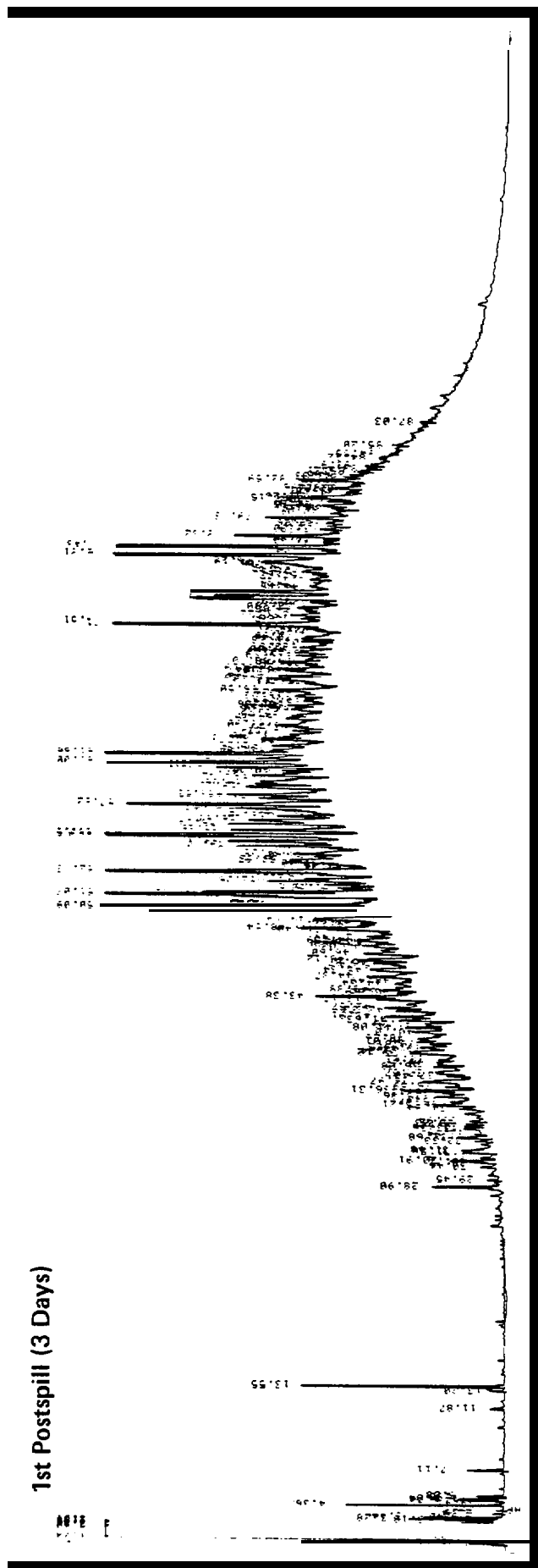**1st Postspill (3 Days)**

2nd Postspill

Figure 3.82. MYA truncata—GC^2 Profiles of Bay 7 Animals (Aromatics).

components decreasing in abundance relative to biogenic
peaks in the two-week samples.

3.4.1.3c Aromatic Hydrocarbon Composition by GC^2/MS

That low levels of a moderately weathered aromatic
hydrocarbon assemblage are found in Bay 7 animals is shown
in Figure 3-83. Very small quantities of naphthalenes
appear in the first (3-day) samples, thereafter being
completely lost from the tissues.   In two weeks, levels of
phenanthrenes and dibenzothiophenes are reduced to roughly
50 percent of their three-day values. The initial levels
of individual aromatics are five to ten times lower than
observed initially in Bays 9 and 10 although the total oil
concentrations are two to three times lower. The two-week
residual aromatic levels (30-150 ppb) in Bay 7 are lower
than those observed from a similar time interval at Bays 9
and 10 (100-700 ppb).   However, the most significant differ-
ence between Bay 7 and other Mya animals (i.e., Bays 9
and 10), other than the lower absolute concentrations in
Bay 7, is the lack of initial abundance of naphthalenes
(i.e., toxic aromatics) in Bay 7 animals indicating either
a loss of naphthalenes during transit of oil from Bay 9 to 7
or an artifact of the slightly later (one to two days later
than Bay 9 and 10) first post-spill samplings.

3.4.1.4 Bay 11

3.4.1.4a Oil Concentrations by UV/F

Background levels of oil, as determined by UV/F, were
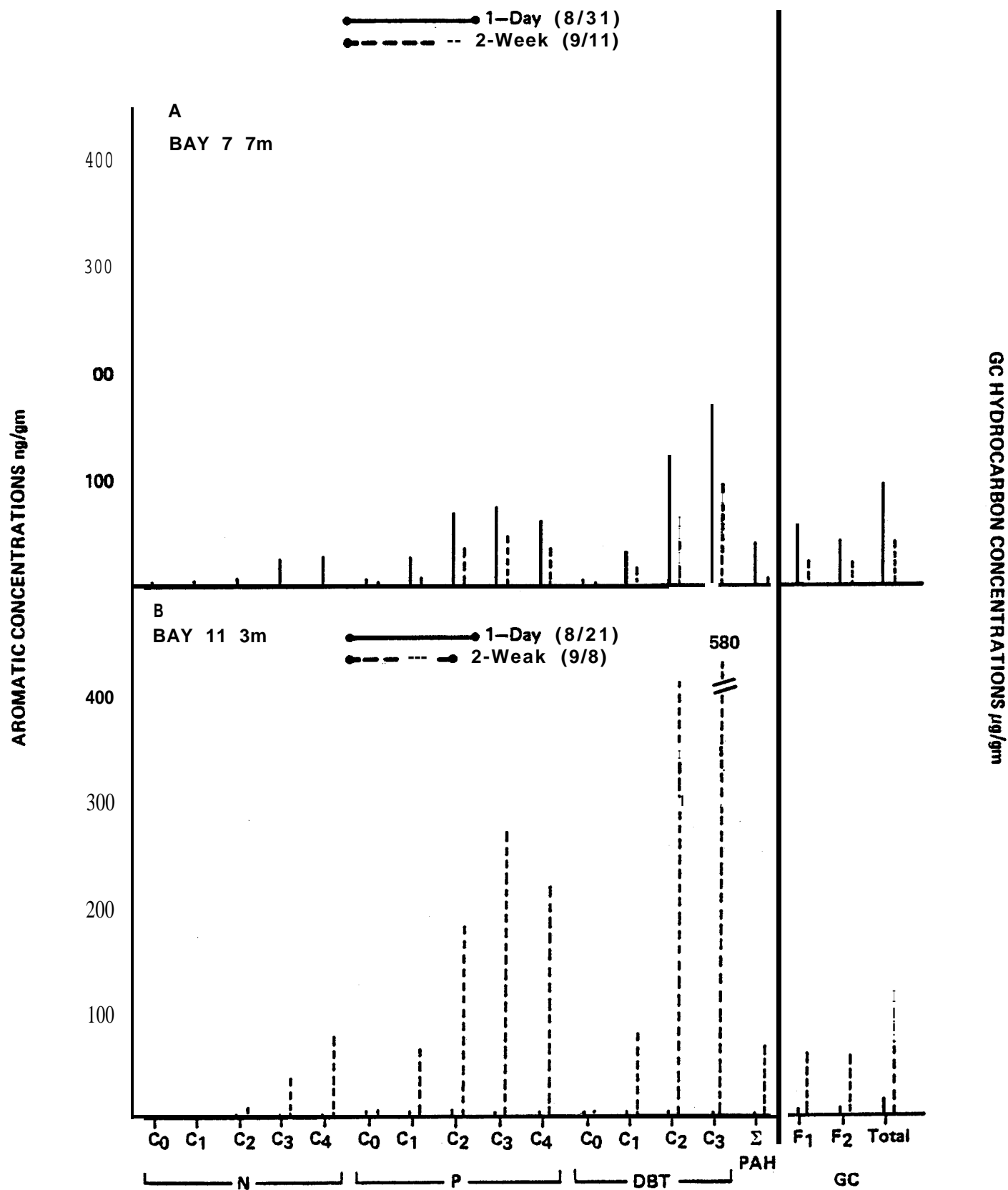found in Bay 11 clams for both the prespill (0.43 [.33, .53] µg/g)

Figure 3.83. _Mya truncata_; Aromatic Profiles of Bays 7 & 11 by GC²/MS.

and the first post-spill periods (2.0 [1.2, 3.1] µg/g) although
the increase (0.4 to 2.0) is statistically significant at
the 95 percent level.   Clams were collected on August 12,
1981 (pre-spill) and August 21 (first post-spill).   Levels
of oil increased to 93 (73, 120) µg/g for the second post-spill
sampling, in clams collected on September 8.   This pattern
is distinctly different from that of the previous bays,
suggesting that the shoreline spill did not impact the
clams until much later, probably due to slower transport
of oil from the shoreline to the benthos.   Concentrations
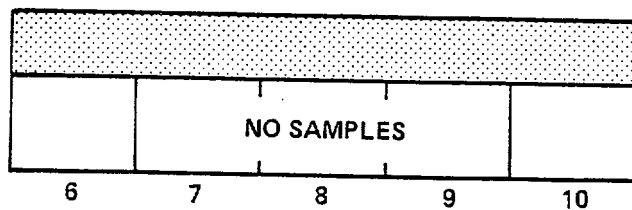are summarized in Figures 3-72 and 3-84.

3.4.1.4b Oil Composition by GC^2

GC^2 results confirm the lack of a detectable oil
impact on Bay 11 Mya prior to the "two-week sampling"
(September 11 = 3 weeks).   The first detectable oil in
these animals was found in the three-week samples and
consisted of a degraded saturated hydrocarbon **assemblage**
(Figure 3-85) and a weathered aromatic assemblage (Fig-
ure 3-86) with residual oil quite evident in the aromatic
fraction.   The alkylated phenanthrene and dibenzothiophene
compounds are characteristic of the residual oil in the
three-week animals.

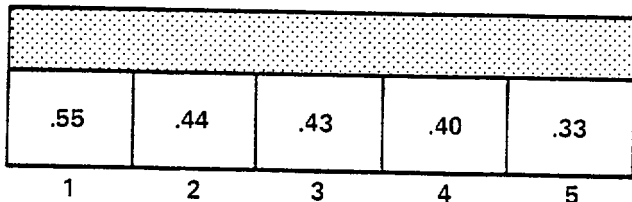### 3.4.1.4c Aromatic Hydrocarbon Composition by GC /MS

GC^2/MS reveals the precise nature of the residual
aromatic assemblage (Figure 3.83).   Substantial quantities
of alkylated phenanthrene (∿200 ppb) and dibenzothiophene
compounds (∿1000 ppb) are revealed in the two-week samples.
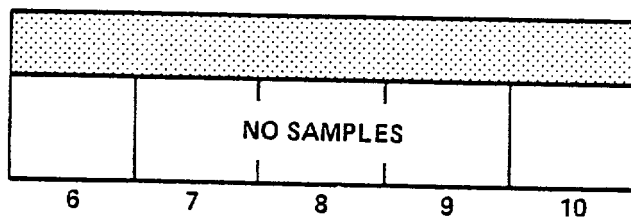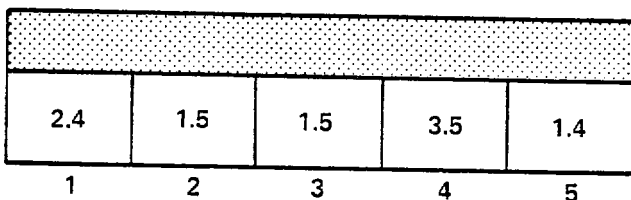This oil is most probably introduced to the Bay 11 benthos

PRESPILL
12 AUG 81

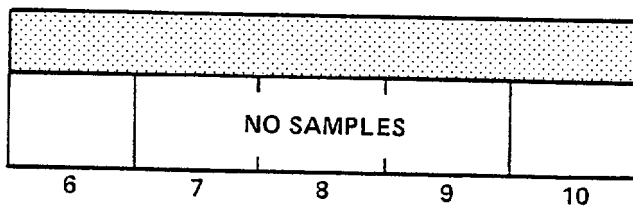|				
		NO SAMPLES		
6	7	8	9	10

T2

.55	.44	.43	.40	.33
1	2	3	4	5

T1

.43 (.33, .53)*

FIRST POSTSPILL
21 AUG 81

		NO SAMPLES		
6	7	8	9	10

T1

2.4	1.5	1.5	3.5	1.4
1	2	3	4	5

T2

2. (1.2,3.1)

SECOND POSTSPILL
8 SEP 81

		NO SAMPLES		
6	7	8	9	10

T1

130.	87.	81.	81.	96.
1	2	3	4	5
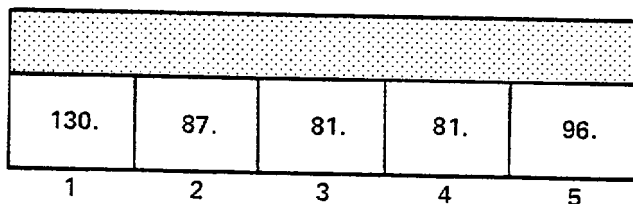
T2

93. (73, 120)

*95% Confidence Limits

Figure 3.84. Concentrations of Oil in Mya truncata, Bay 11 by UV/F (µg/g).

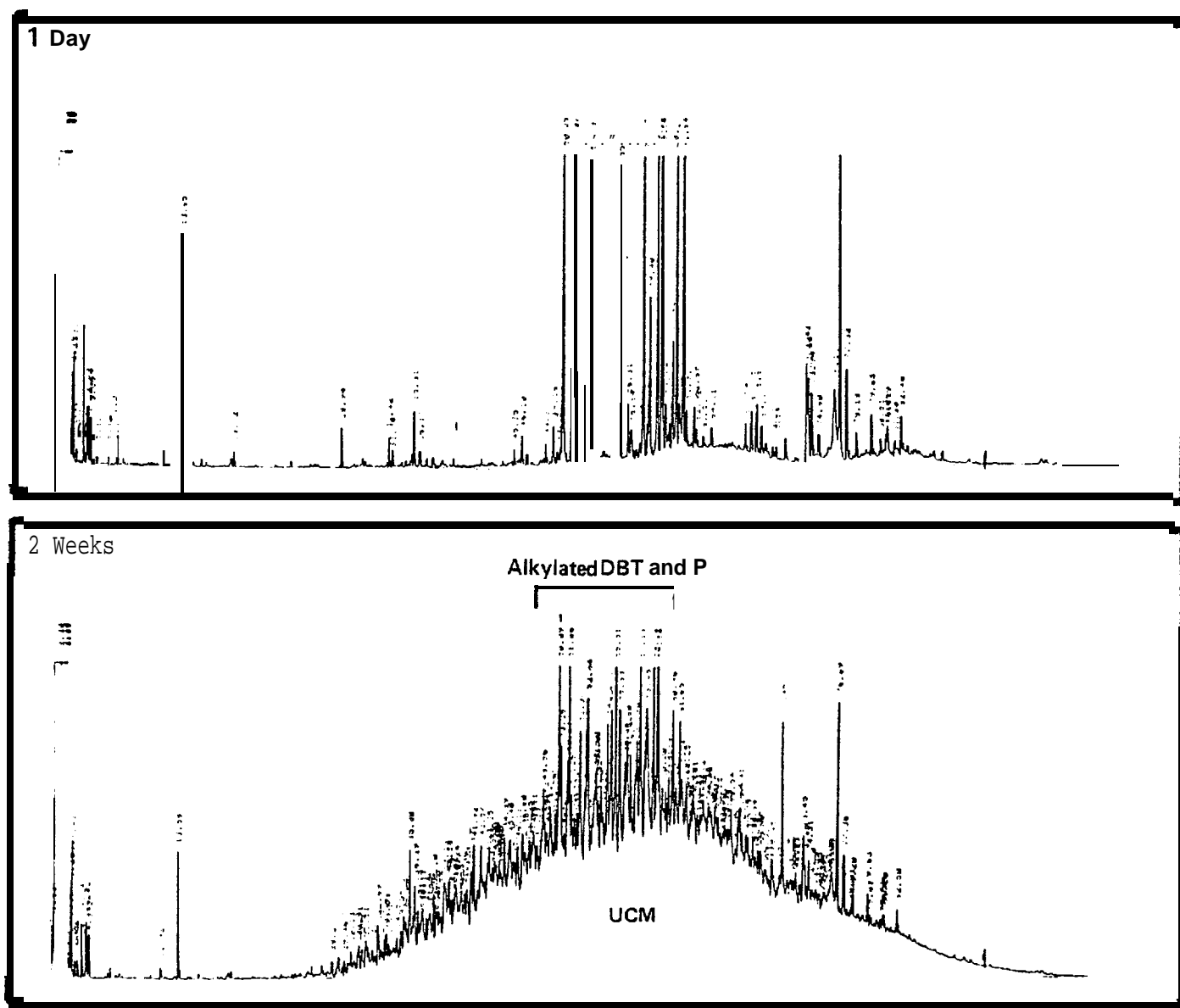Figure 3.85. **MYA truncata** -Bay 11 (Saturates).

Figure 3.86. MYA truncata -Bay 11 (Aromatics).

through beach erosion processes, but the influence of intrusion of dispersed oil residues between August 21 and September 11 cannot be assessed from these data alone.

3.4.1.5 UV/F vs. GC Analysis

UV\F data from each tissue plot station was weight averaged to obtain an oil concentration for each stratum, and compared by linear regression to data obtained by GC^2. UV/F concentrations are equivalent to 1.06 GC (f_1 + f2) concentrations with a correlation coefficient of 0.89. Prespill, first and second postspill are all included in this graph (Figure 3.87).   Individual tissue plot stations analyzed by both UV/F and GC are also graphed.   For all species, UV/F analysis was found to be roughly comparable to GC analysis (slope of the line), with a correction for background (y-intercept) and regardless of the concentration of oil.   Individual tissue plot stations 1,3, and 5 were taken from Bay 9, second postspill, and averaged 42.3 μg/g oil as compared to the composite 7m stratum concentration of 57.2 μg/g oil.

3.4.1.6 Individual Mya Animals

Single Mya animals were individually analyzed (~15 g each wet weight) to assess clam to clam variation within a tissue plot station.   Mya tissue plot stations generally contained 10-25 clams, which were homogenized, and a 30 g wet weight subsample analyzed.   UV/F and GC^2 data are compared in Table 3-21.   As can be seen, the correlation of UV/F data for Bay 7 clams from the individual animal (107 μg/g oil) within the tissue plot station (60 μg/g
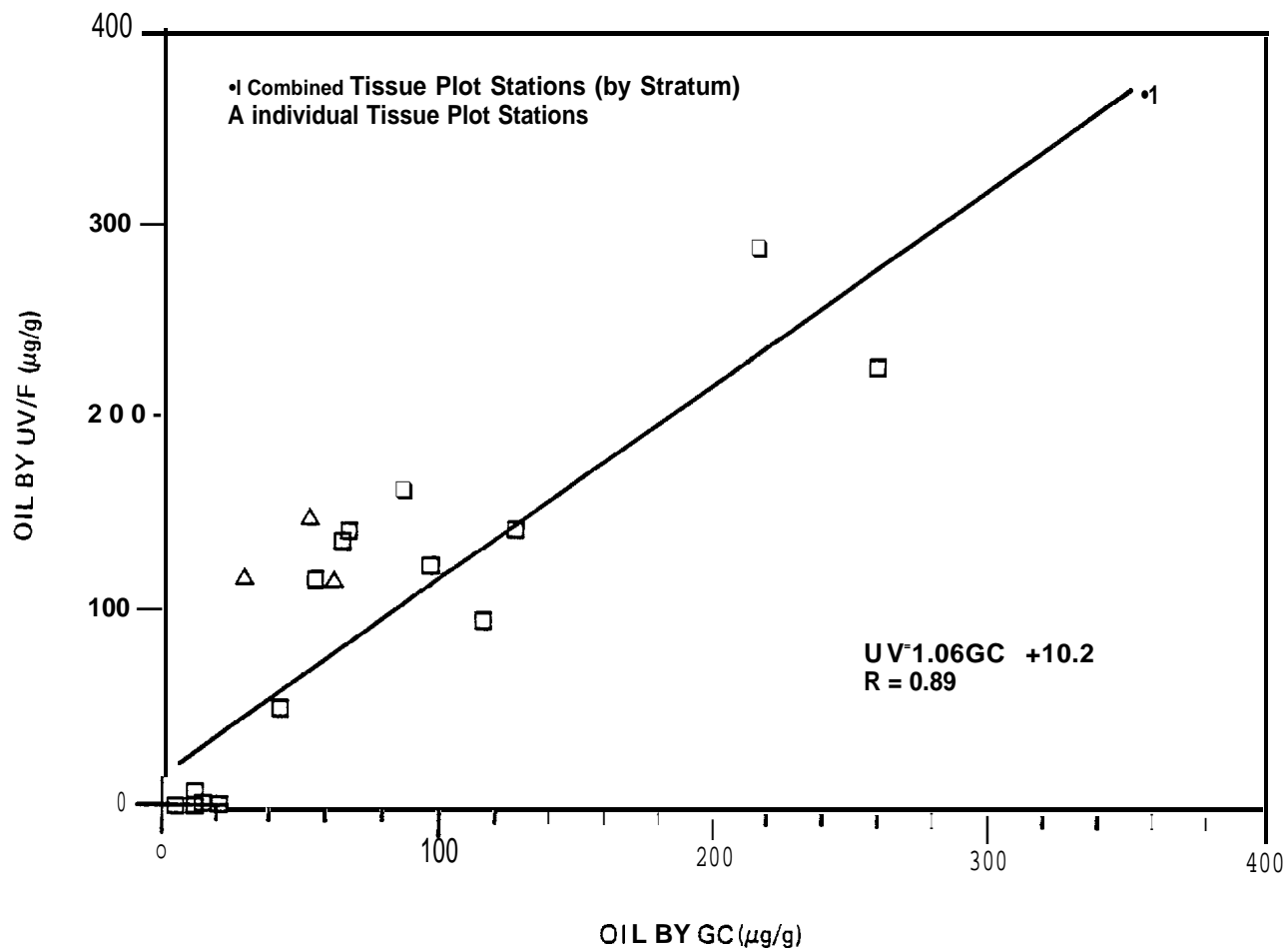
Figure 3.87. Regression of *Mya* UV/F vs GC² Data.

oil) to the stratum average (stations 1-5, 114 µg/g oil)
is reasonable. The individual clam concentrations are
higher than those for the entire stratum (Table 3-24), but
may be a reflection of the analysis of only five individuals
as opposed to the many *more* individuals that comprise
a stratum GC^2 result (∿100). On the other hand, Bay 9
clams show good correlation between the individual animal
and the composite stratum GC^2 oil concentrations.

3.4.2 Serripes groenlandicus

UV/F analyses were performed on a total of 63 samples
including individual tissue plot stations (handpicked or
airlifted), pooled dissected guts and remaining tissue from
an extra Bay 10 animal set.

GC^2 analyses were conducted on pooled extracts from
each stratum (15), on the guts and muscle samples (2) and
on the individual tissue plot stations (3).

3.4.2.1 Bay 9

3.4.2.1a Oil Concentrations by UV/F

Serripes UV/F data (Figures 3-88 and 3-89) illustrate
similar trends to those for Mya. Pre-spill concentrations
in Bay 9 were 0.68 (-.02, 1.9) g/g. First postspill concentra-
tions were higher than Mya, reaching 482 (340, 680) µg/g
(airlift) and 186 (110, 330) (handpicked). An analytical
triplicate sampling for this stratum (Station 3) was 556±119 µg/g,
see Section 2.2.9). Second post-spill concentrations for the
7m stratum were 97 (59, 160) µg/g (handpicked) and 116.0

TABLE 3-24

INDIVIDUAL MYA CLAMS

	MYA, BAY 7, STATION 2 FIRST POSTSPILL (µg/g)		MYA, BAY 7, STATION 2 FIRST POSTSPILL (µg/g)	
CLAM	UV/F	GC [2]	UV/F	GC [2]
1	100	**145.6**	**43**	
2	**34**	**119.8**	**79**	**162.4**
3	200	350.1	76	84.4
4	**96**	**240.1**	**99**	**180.3**
5			**98**	**109.7**
	107[a]	**213.9**	79	**134.2**
Tissue Plot Station 2 UV/F	60		195	
Weight Averaged Stratum UV/F	114		121	
Composite Stratum GC 2		96.7		126.8

arithmetic mean.
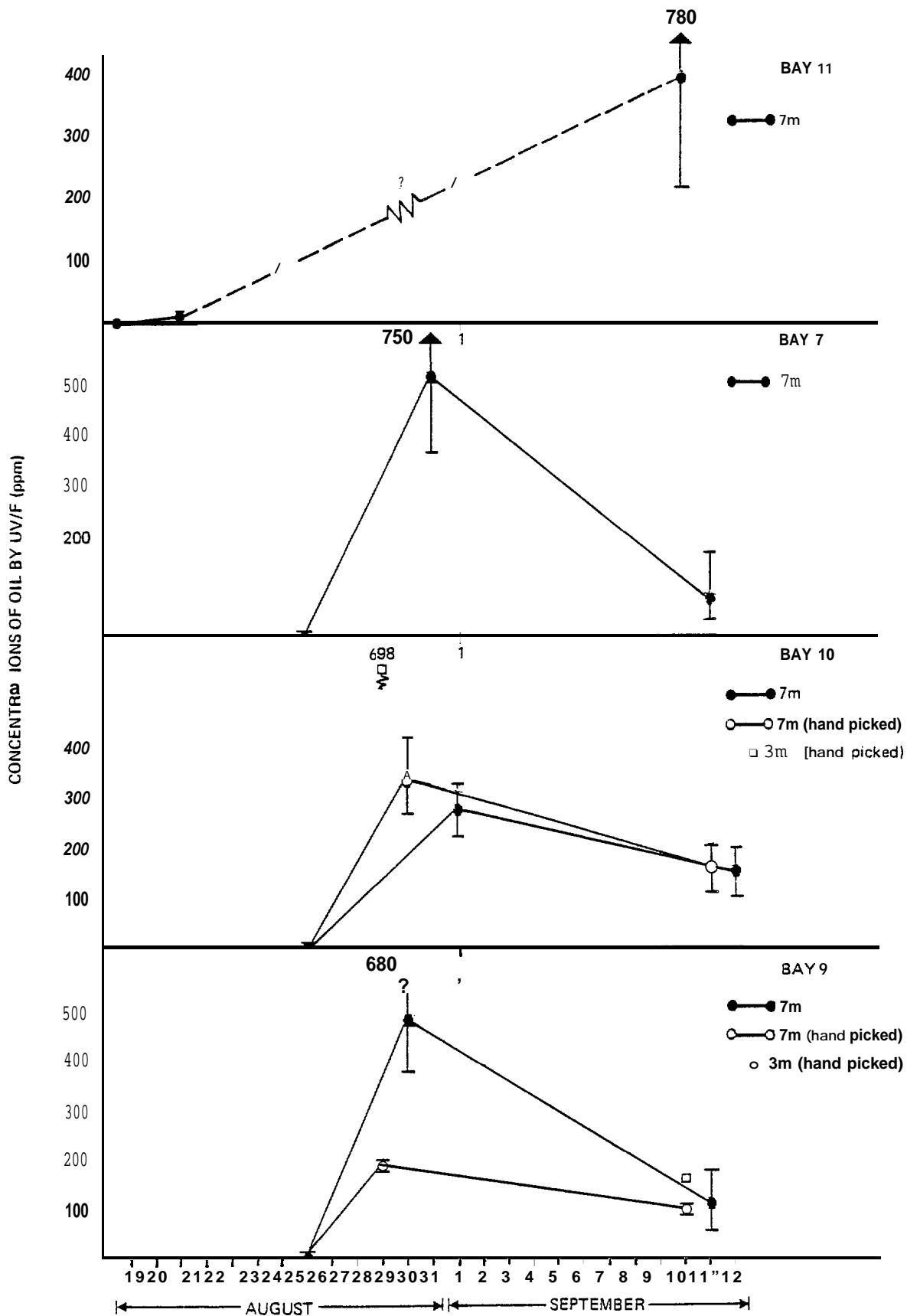
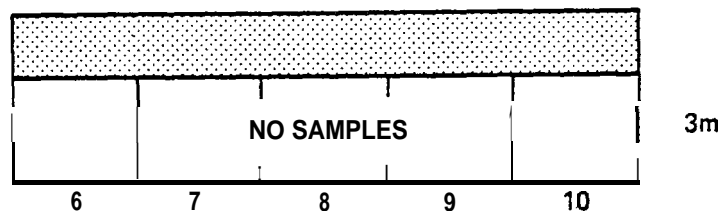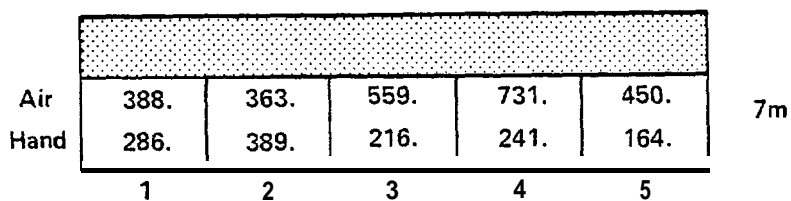Figure 3.88. *Serripes groelandicus* Concentration Summary.
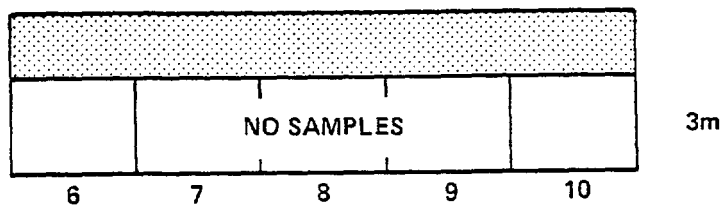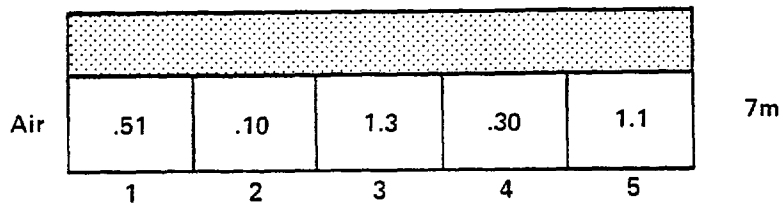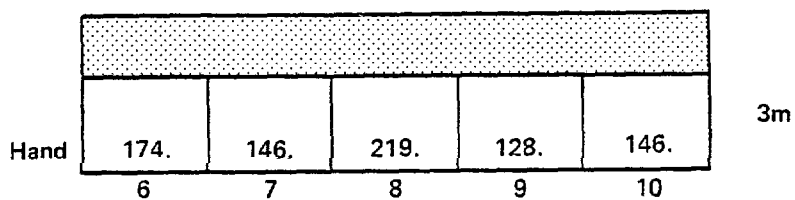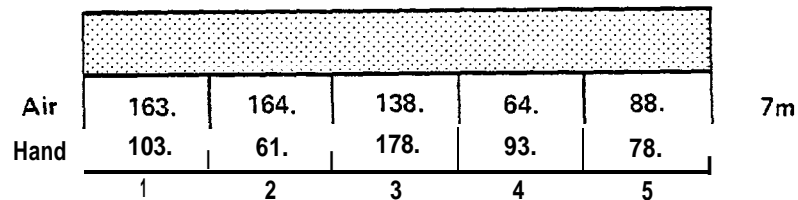
Figure 3.89, Concentrations of Oil in Serripes, Bay 9 by UV/F (µg/g).

(69,190)(air lifted).   Clams from the 3m stratum contained 160
(120, 210) μ g/g of oil (hand picked). Bay 9 first postspill
data is the only bay and time in which airlift vs. hand-picked
clams were found to contain significantly different concentra-
tions of oil.

3.4.2.1b OilComposition by GC^2

Beginning with a **pre-spill** hydrocarbon assemblage
consisting of **biogenic** molecules, Serripes acquires nearly a
full range of saturated and aromatic hydrocarbons from the
oil (Figures 3-90 and 3-91), although somewhat depleted in
the **naphthalene** component series.   As with **Mya,** the saturated
hydrocarbon assemblage in the C_{13} to C_{22} range is substan-
tially degraded in the second post-spill sampling (Figure
3-85).   However, a secondary saturated distribution persists
in an undegraded form in the C23 to C33 range, including
a secondary **UCM** in this boiling range.   Thus, the GC^2
profiles of the residues in the second post-spill sampling
differ significantly from the **Mya** profiles with respect to
the retention of this higher-molecular-weight material.

3.4.2.1c Aromatic Hydrocarbon Composition By GC^2/MS

Another substantial difference between **Mya** and Serripes
behavior **vis-a-vis** petroleum component retention is revealed
in the GC^2/MS data (Figure 3-91).   The first post-spill
sampling consists largely of **naphthalene** compounds which
are completely absent in the second post-spill sampling
from the 7m stratum, but still abundant in the 3m stratum.
However, levels of phenanthrenes and dibenzothiophenes
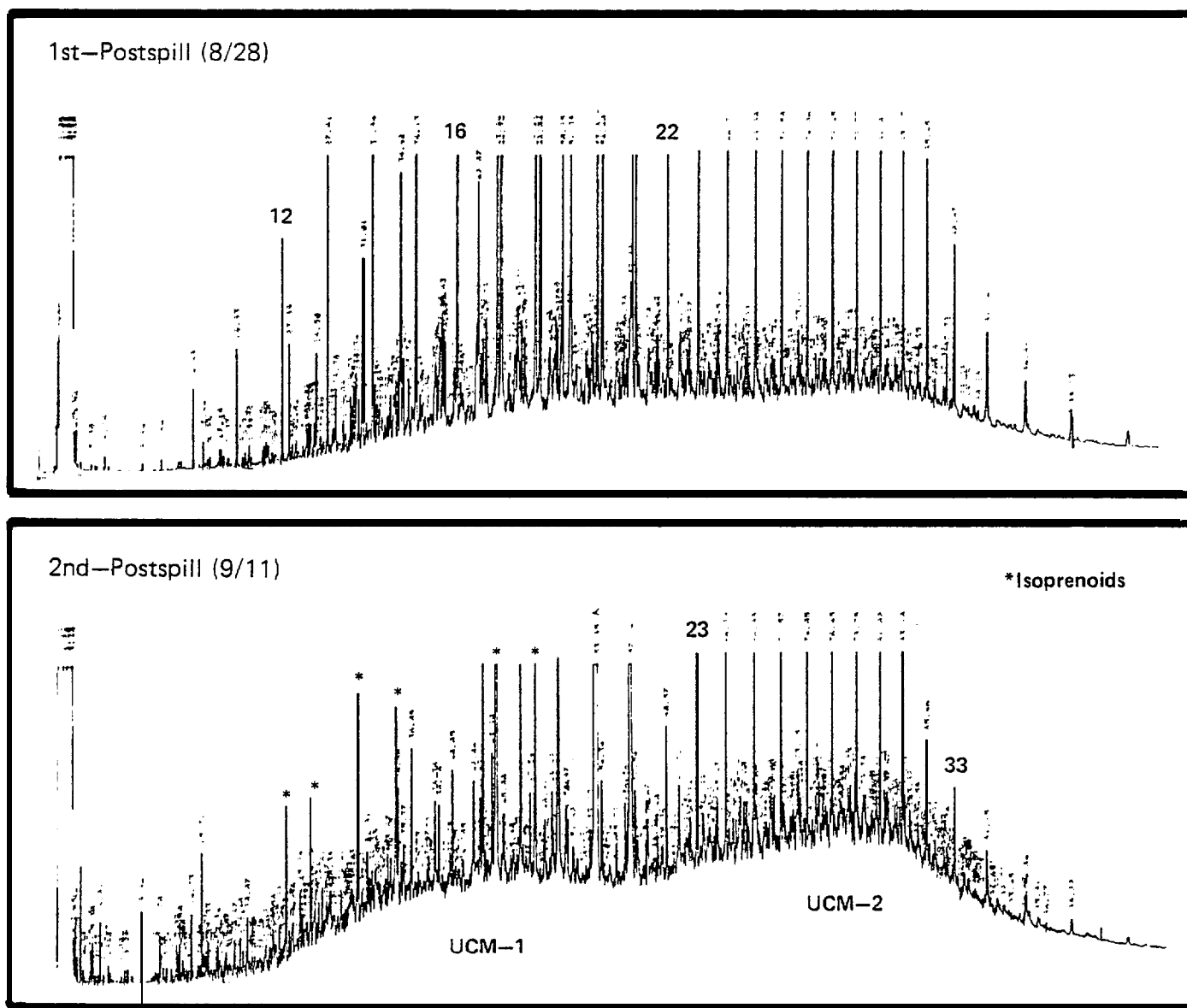persist and no apparent deputation of these compound

Figure 3.90. *Serripes green/andicus-GC²* Profiles of Bay 9 Animals (Saturates).
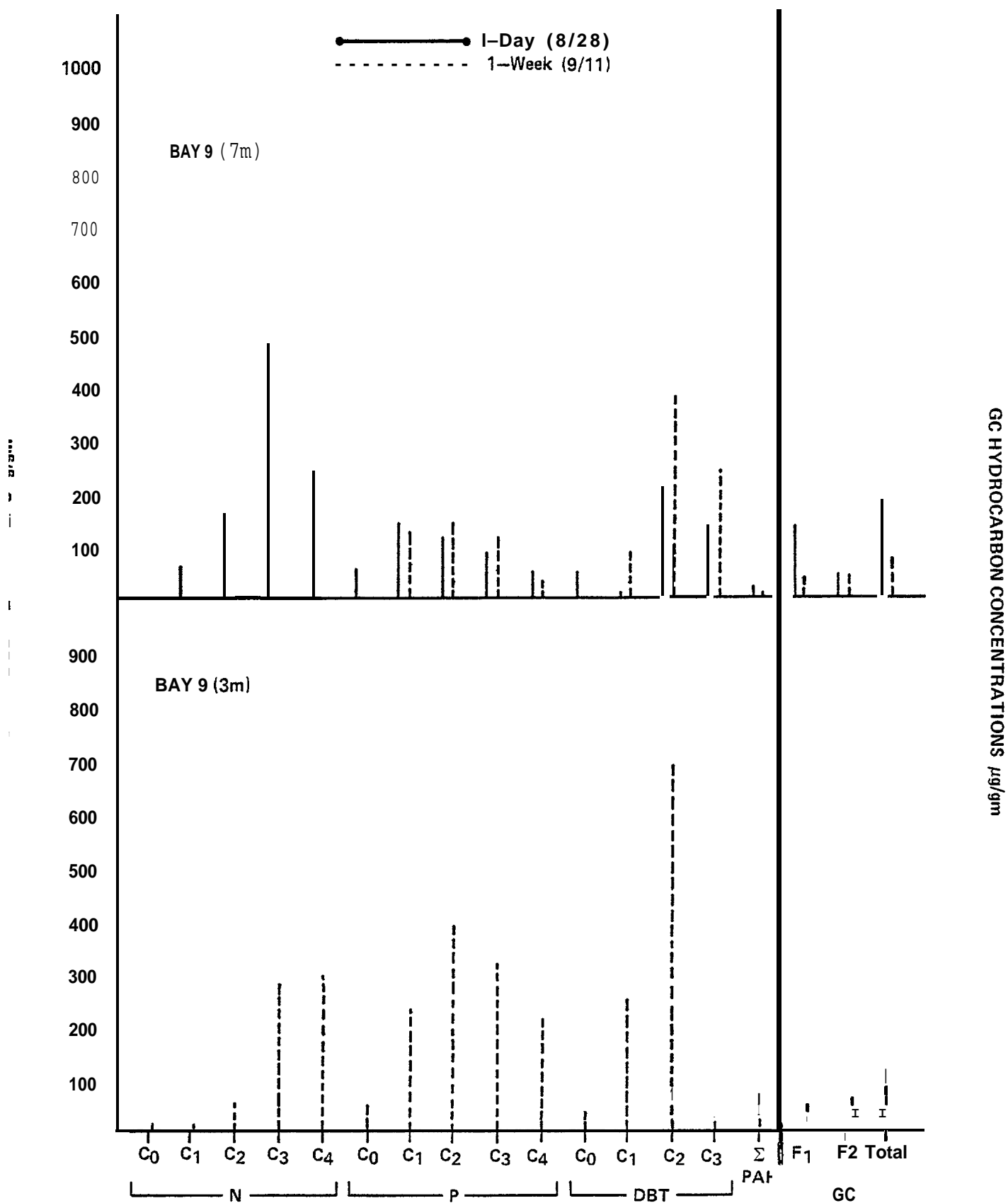
Figure 3.91. Serripes Aromatic Profiles (by GC^2/MS).

series occurs (Figure 3-91).   Indeed, levels may be increas-
ing.   The GC^2/MS profiles of the nearshore (3m) transect
indicate little compositional change in that **naphthalenes**
and C_0 and C_1 phenanthrenes persist.   This finding illus-
trates that Serripes as a species certainly retains more
of the potentially harmful aromatic hydrocarbons than does Mya.

3.4.2.2 B a y   1 0

3.4.2.2a Oil Concentrations by UV\F

Prespill oil concentrations (Figure 3-88 and 3-92) were
1.4 (**.40**, 3.0) µg/g. **First** **postspill** concentrations from   the
7m stratum were 329 (240, 460) µg/g (hand picked) and 278
(220, 350) µg/g (air lift), and from the 3m stratum 698 (500,
970) (hand picked).   Second **postspill** concentrations for the 7m
stratum decreased to 141 (110, 180) (hand picked) and 149 (130,
170) (air lifted).   A single tissue plot was collected from the
3m stratum and contained 177 µg/g of oil.   There was no
statistical difference between airlift or handpicked sampled
from Bay 10 (Appendix A).   All differences in concentrations
of oil measured at each time period, and between strata are
significant for the Serripes clam.   Serripes concentrations
are higher than Mya initially **but reach** similar **levels** after
two weeks.

3.4.2.2b Oil Composition by GC^2

Bay 10 trends in petroleum profiles for Serripes are
identical to those observed in Bay 9.   Levels of hydrocarbons
are somewhat higher for the Bay 10 Serripes, especially for
the 3m stratum (an observation made on Mya as well), but

TISSUE
PLOTS

NO SAMPLES   3m

Air   1.6   .8   .6   3.6   1.1   7m   1.4 (.40, 3.0)*

        1   2   3   4   5

FIRST POSTSPI LL
29 AUG–1SEP 81

Hand   499.   996.   656.   814.   629.   3m   698.

        6   7   8   9   10

                                                       30 AUG 81

Air   302.   296.   314.   294.   199.   278. (220, 350)
Hand   295.   302.   302.   296.   451.   7m   ─────────────
                                                       329. (240, 460)

        1   2   3   4   5

SECOND POSTSPI LL
11-12 SEP 81

Hand   177.   — | | | 3m   177,

        6   7   8   9   10

Air   146.   157.   135.   135.   372.   149. (130, 170)
Hand   124.   139.   —   172.   134.   7m   ─────────────
                                                       141. (110, 180)

        1   2   3   4   5

*95% Confidence Limits
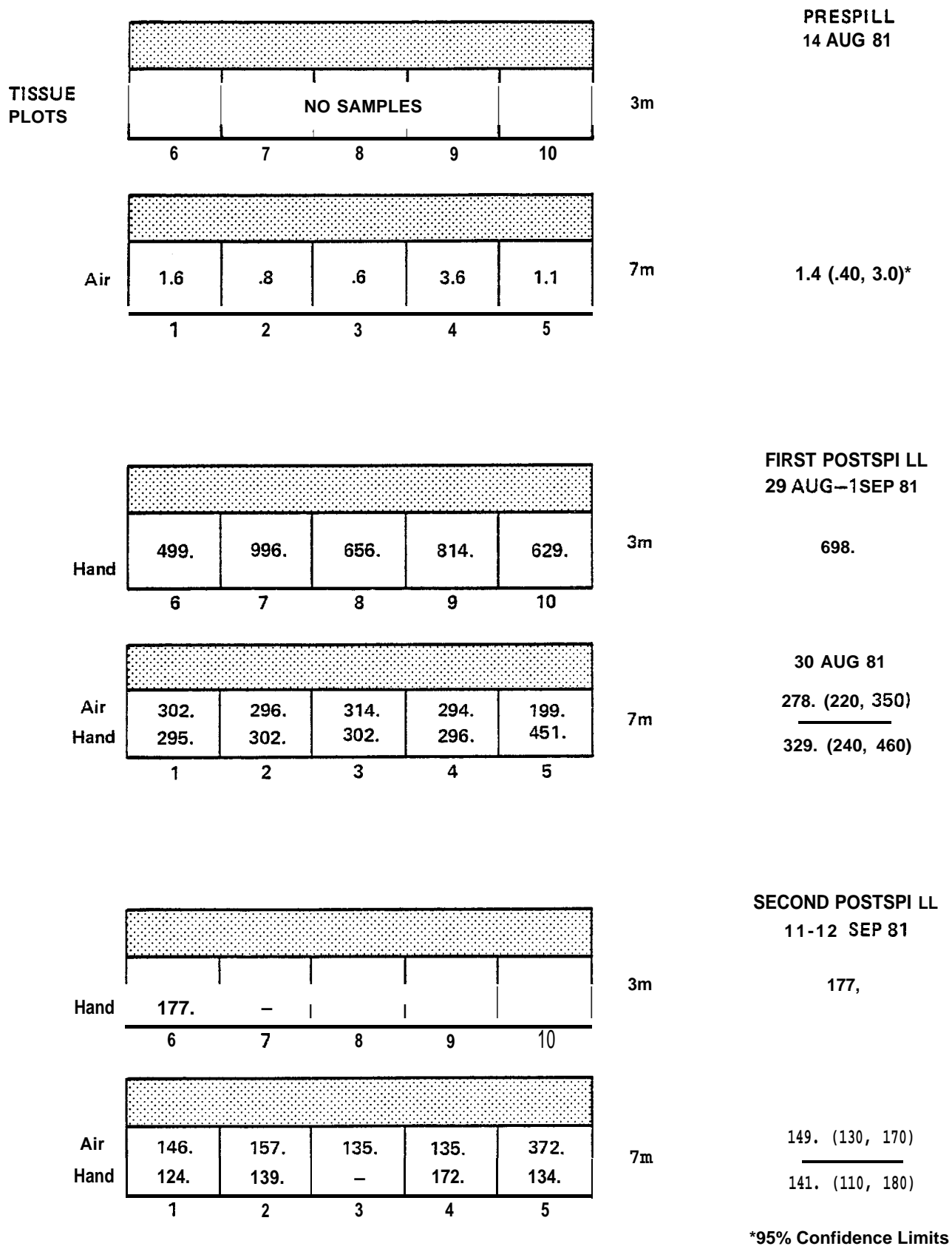
Figure 3.92. **Concentrations of Oil in Serripes, Bay 10 by** UV/F(μg/g).

compositionally Serripes from Bays 9 and 10 behave similarly
(Figure 3-93). The retention of higher molecular weight
saturates again differentiates Mya from Serripes at the same
location.

3.4.2.2c Aromatic Hydrocarbon Composition by GC^2/MS

Serripes from Bays 9 and 10 behave similarly with respect
to aromatic hydrocarbon profiles. An abundance of naphthalene
compounds initially acquired is still present in the second
sampling (September 11) (Figure 3-94) and levels of phenanthrenes
and dibenzothiophenes are at least as abundant as in the first
post-spill sampling (September 1). Note that the abundance of
the total f_2 fraction both in the Bay 10 7m set (Figure 3-94)
and in the Bay 9 3m set remains nearly constant in spite of
a lowering of the f_1 fractions by either deputation or deg-
radation. The reason for this differential behavior of the f_1
and f_2 fractions remains unknown.

A very large quantity of naphthalenes (2-4 ppm) and other
aromatics characterizes the September 1 sample of Serripes
taken at the 3m stratum in Bay 10.

3.4.2.3 Bay 7

3.4.2.3a Concentrations of Oil by UV/F

Three of five tissue plot stations sampled during the
pre-spill period contained enough Serripes for analysis.
Concentration levels were in 1.2 (1.2, 1.3) µg/g oil equivalents.
First post-spill clams contained 517 (360, 750) µg/g oil, much
higher than Mya clams from the same stations. Second post-spill
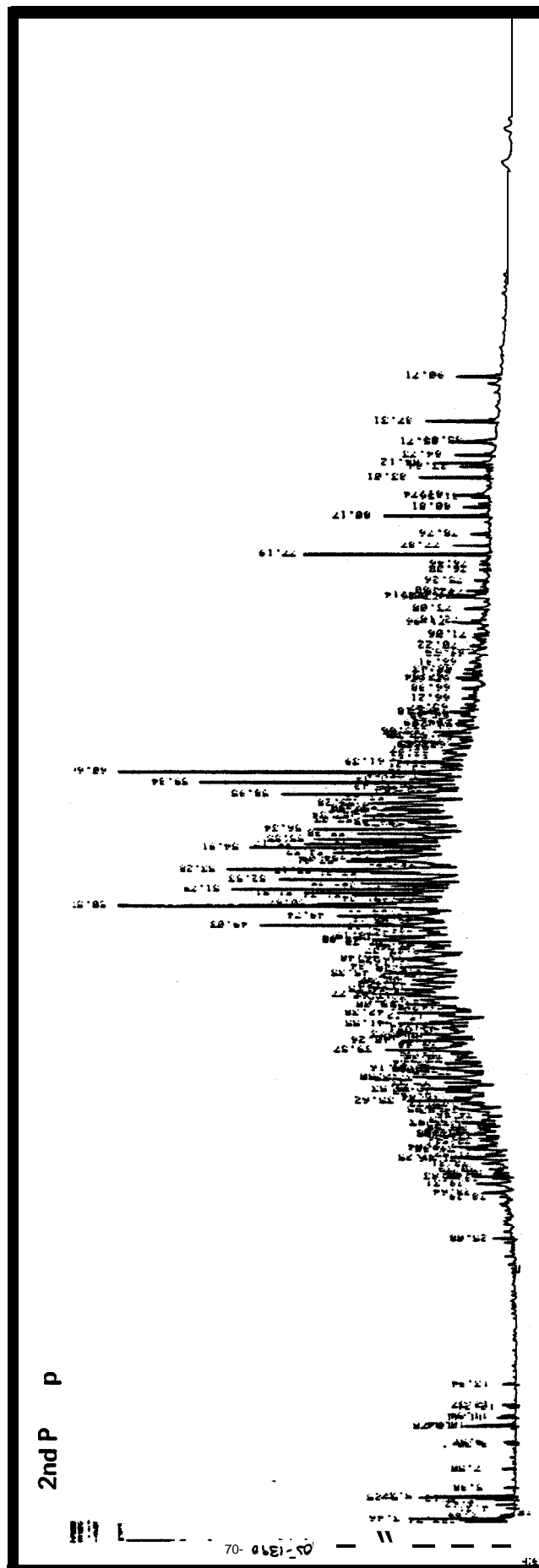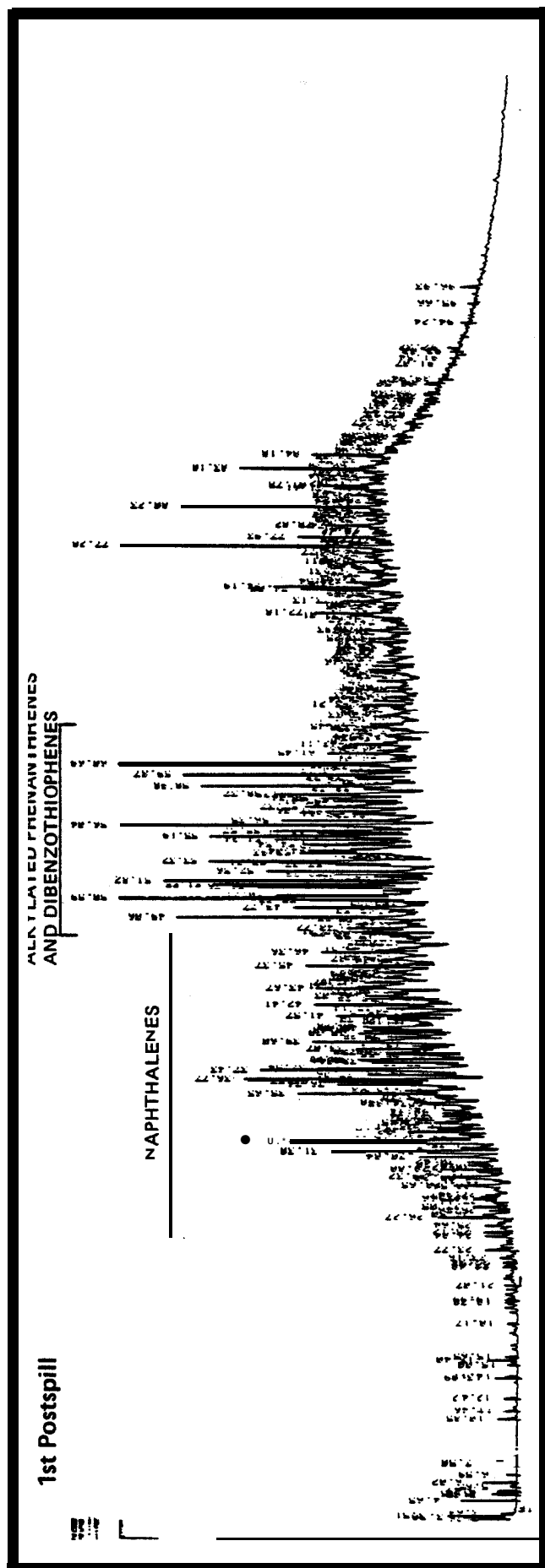
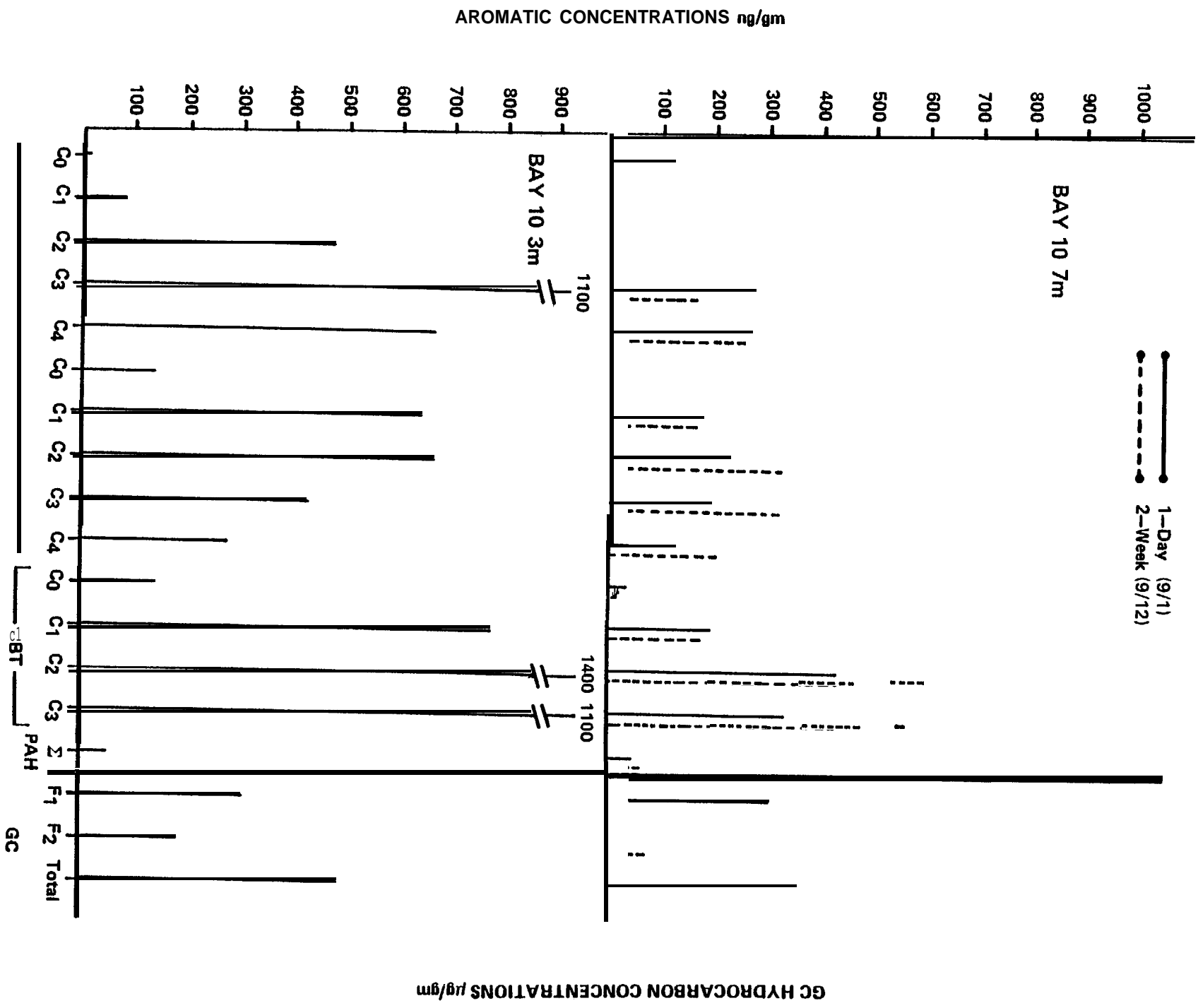Figure 3.93. Aromatic Hydrocarbons in Serripes—Bay 0, 3 Meters).

AROMATIC CONCENTRATIONS ng/gm

GC HYDROCARBON CONCENTRATIONS µg/gm

Figure 3.94. _Serripes_ Aromatic Profiles.

-24.-

clams had depurated over 75% of this oil to 73 (31, 170) tg/g oil (see Figures 3-88 and 3-95). All differences are significant for <u>Serripes</u> in Bay 7. (See Appendix A.)

3.4.2.3b   <u>Oil Composition by GC2</u>

Initially Bay 7 **<u>Serripes</u>** contained equal or greater quantities of oil than did eit-her of the dispersed oil test bays. Just as Bay 10 animals initially (August 29) contained higher levels of oil than the Bay 9 animals (August 28), the higher initial **levels** of Bay 7 <u>Serripes</u> (August **31)** may reflect increased uptake during the **August** 28 to August 31 period. The GC2 profile of the earliest sampled animals **(9/1)** revealed oil in the process of being degraded **(ALK/ISO=0.2)** and a smaller amount of oil of a similar composition 10 days later (September 11). The marked abundance of higher boiling saturates seen with heavier water column dosings at Bays 9 and 10 are not apparent on the Bay 7 traces. However, aromatic hydrocarbon profiles at the second post-spill sampling do resemble those from the test bays, albeit at **lower** concentrations (Figure **3-96).**

3.4.2.3c <u>Aromatic Hydrocarbon Compositions by. GC^2/MS</u>

Again, individual aromatic levels do not decrease during the first two weeks, in spite of a substantial loss of the f2 fraction as a whole. Phenanthrene and dibenzothiophene compounds persist at initial **levels** (Figure 3-97), while the small amount of naphthalenes originally acquired, "disappears."

PRESPILL
17 AUG 81

TISSUE
PLOTS

6	7	8	9	10
		NO SAMPLES		

3m

Air

1	2	3	4	5
—	—	1.2	1.2	.9
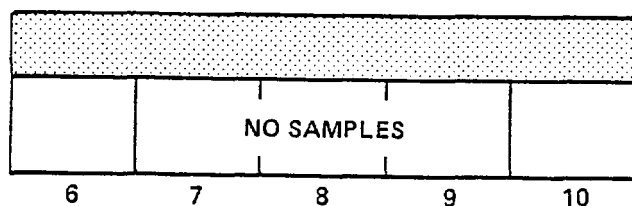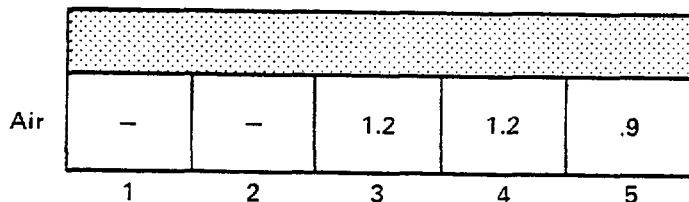
7m   1.2 (1.2, 1.3)*

FIRST POSTSPI LL
1 SEP 81

6	7	8	9	10
		NO SAMPLES		

3m

Air

1	2	3	4	5
—	623.	376.	603.	512.
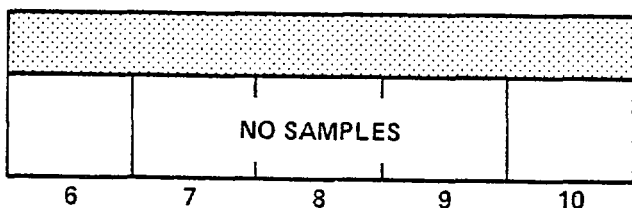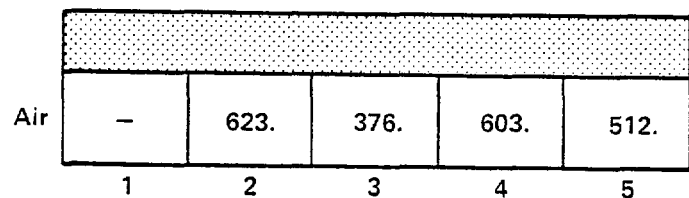
7m   517. (360, 750)

SECOND POSTSPILL
11 SEP 81

6	7	8	9	10
		NO SAMPLES		

3m

Air

1	2	3	4	5
—	99.	119.		36.
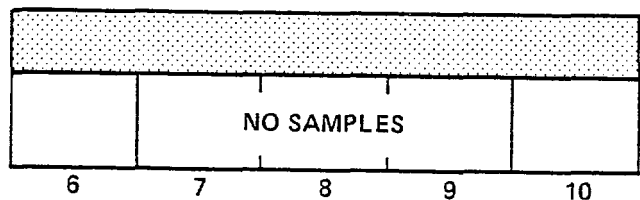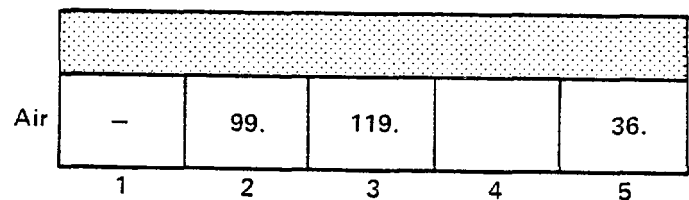
7m   73. (31, 170)

* 95% Confidence Limits

Figure 3.95. Concentrations of Oil in Serripes, Bay 7 by UV/F (μg/g).

Pre-Spill

2nd—Postspill (9/' 1)

Alkylated Phenanthrenes/Dibenzo Thiophenes

Figure 3.96. <u>Serripes</u>—Bay 7 (Aromatics).
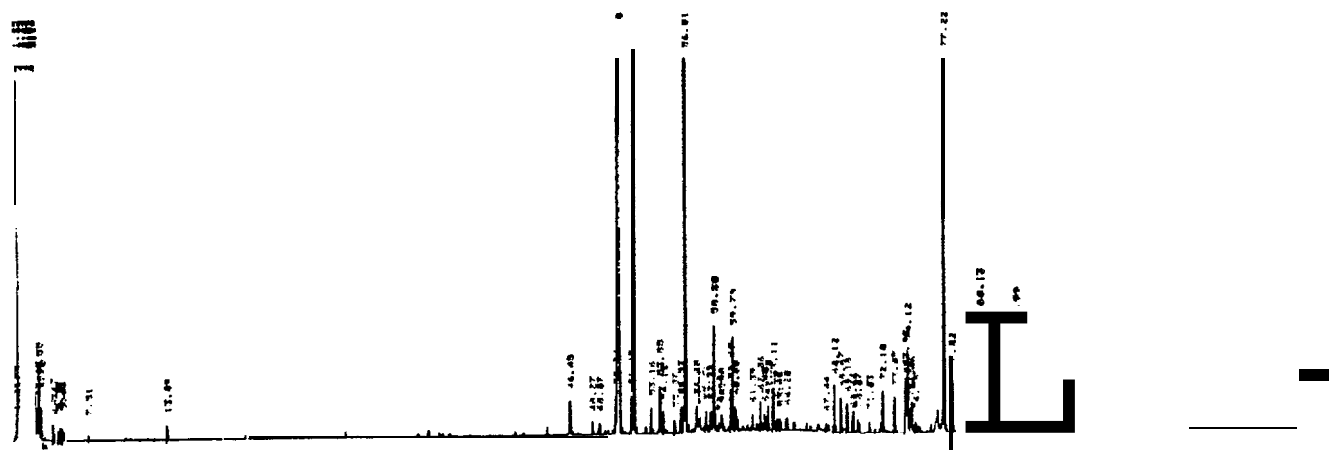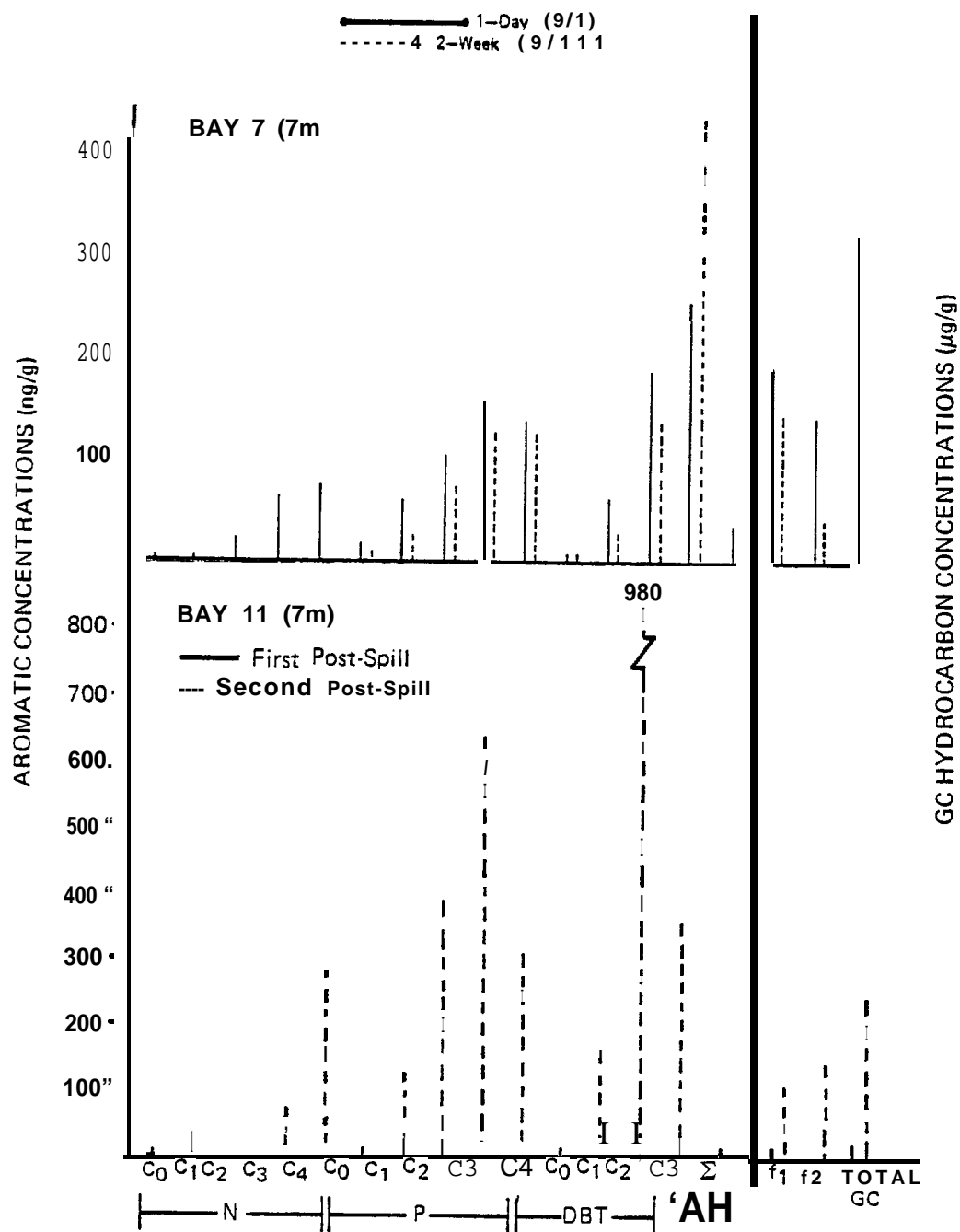
Figure 3.97. Aromatic Hydrocarbon Profiles in *Serripes* by GC^2/MS (Bay 7 and 11).

3.4.2.4 Bay 11

3.4.2.4a Oil Concentrations by UV/F

Serripes were found only at Station 3 during the
pre-spill: 1.6 µg/g oil. First post-spill clams contained
6.0 (.19, 41) g/g of oil, and the three tissue plot stations
in which clams were found during the second post-spill sampling
contained 394 (200, 780) µg/g oil. These clams follow the
same pattern as Mya for Bay 11, that is an initial low but
significant increase in oil followed by a large increase in
the 3-week (second post-spill) sampling (see Figures 3-88
and 3-98).

3.4.2.4b Oil Composition by GC^2

Representative GC^2 traces of Bay 11 Serripes (Fig-
ures 3-99 and 3-100) are consistent with observations for
other bays with respect to (1) degradation of lower boiling
n-alkanes with time, and relative retention of branched
and isoprenoid alkanes; (2) the retention of intact n-C_{23}
to n-C_{33} alkanes; and (3) the presistence of alkylated
phenanthrene and dibenzothiophene compounds. GC^2 analyses
did not detect any petroleum present in the first post-spill
sampling (August 21) in spite of small increases in UV/F-
determined "oil equivalents" levels.

3.4.2.4c Aromatic Hydrocarbon Compositions by GC^2/MS

The first and second postspill Bay 11 Serripes 7m
stratum composites were analyzed by GC^2/MS. Results
in Figure 3.97b indicate that no detectable aromatics were
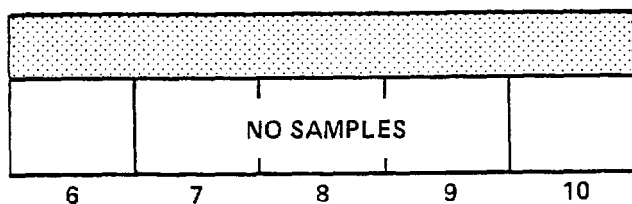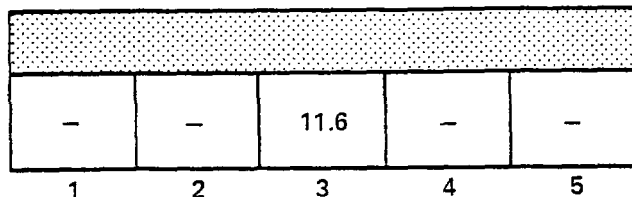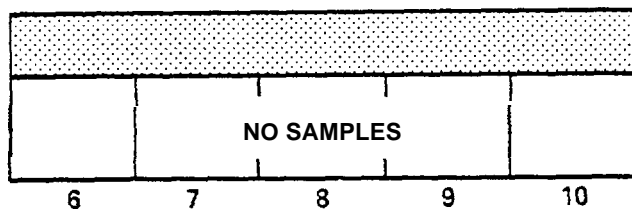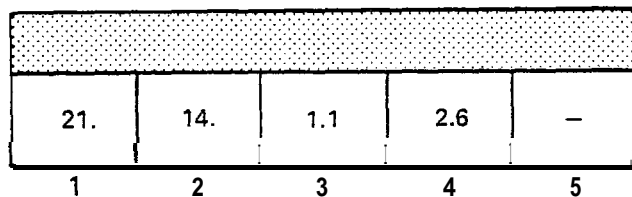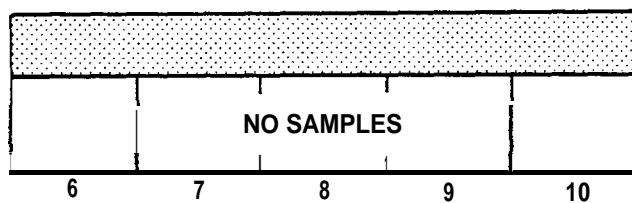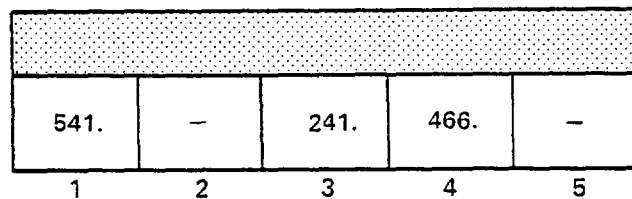
Figure 3.98. Concentrations of Oil in Serripes, Bay 11 by UV/F (μg/g).

Pre-Spill

2nd—Postspill (9/11)

*Isoprenoids
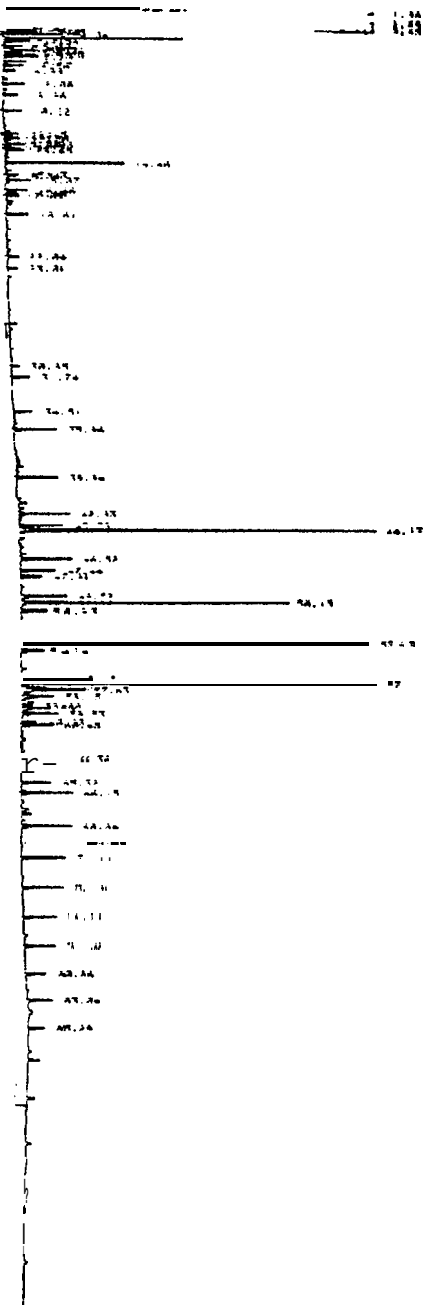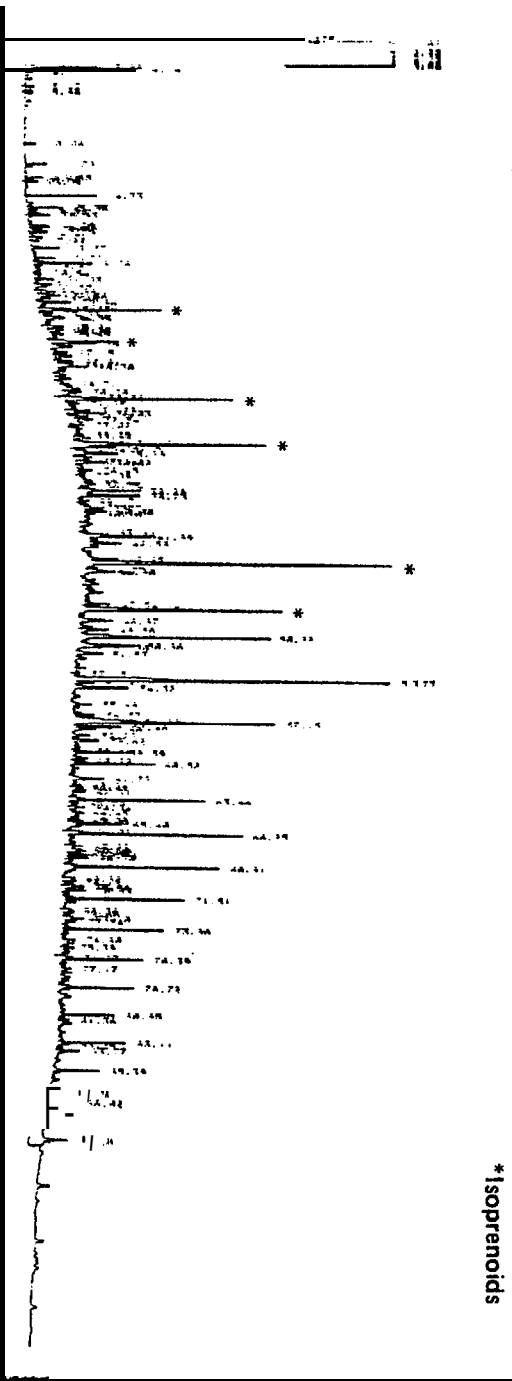
Figure 3.99. Serripes—Bay 11 (Saturates)
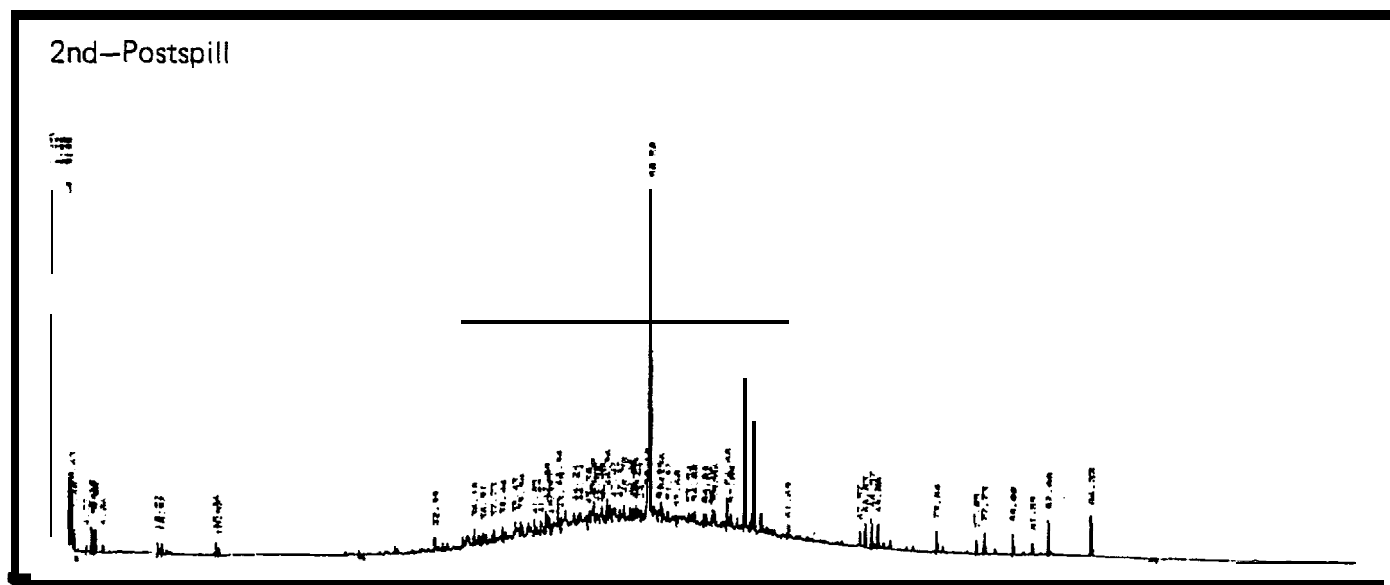
2nd—Postspill

Figure 3.100. Serripes—Bay 11 (Aromatics).

present in the animals initially and that concentrations of
all aromatics increased during the next three weeks. The
residual aromatics composition is typical of second post-
spill Serripes samples.

3.4.2.5 UV/F VS. GC^2 Analyses

As with Mya, Serripes data for GC^2 and weight averaged
UV/F by stratum was plotted to correlate UV/F oil concentra-
tions with GC^2 oil concentrations. UV/F data was equivalent
to 1.40 (GC^2 data) - 20.6 (Figure 3.101). Hence, for this
species, the GC^2 data contained a higher non-oil background
level than the UV/F data. Figure 3.101 also illustrates the
correlation between UV/F and GC^2 for all concentrations of
oil (compare lines plotted with and without prespill samples).
Individual tissue plot stations fall reasonably close to the
line, again indicating a consistency between individual and
combined tissue plot analyses. Tissue plot stations 1, 3,
and 5 were taken from Bay 9 first postspill and averaged
163.0 µg/g of oil as compared to the composite 7m stratum
mean of 182.0 µg/g.

3.4.2.6 Separate Analyses of Serripes Gut and Muscle Tissue

A collection of hand-picked Serripes from Bay 10 was
collected following the spill (August 30). Nine individual
organisms were dissected, the gut removed from the bulk
muscle tissue, and the gut and residual tissue analyzed
separately. GC^2 and GC^2/MS analyses were performed.
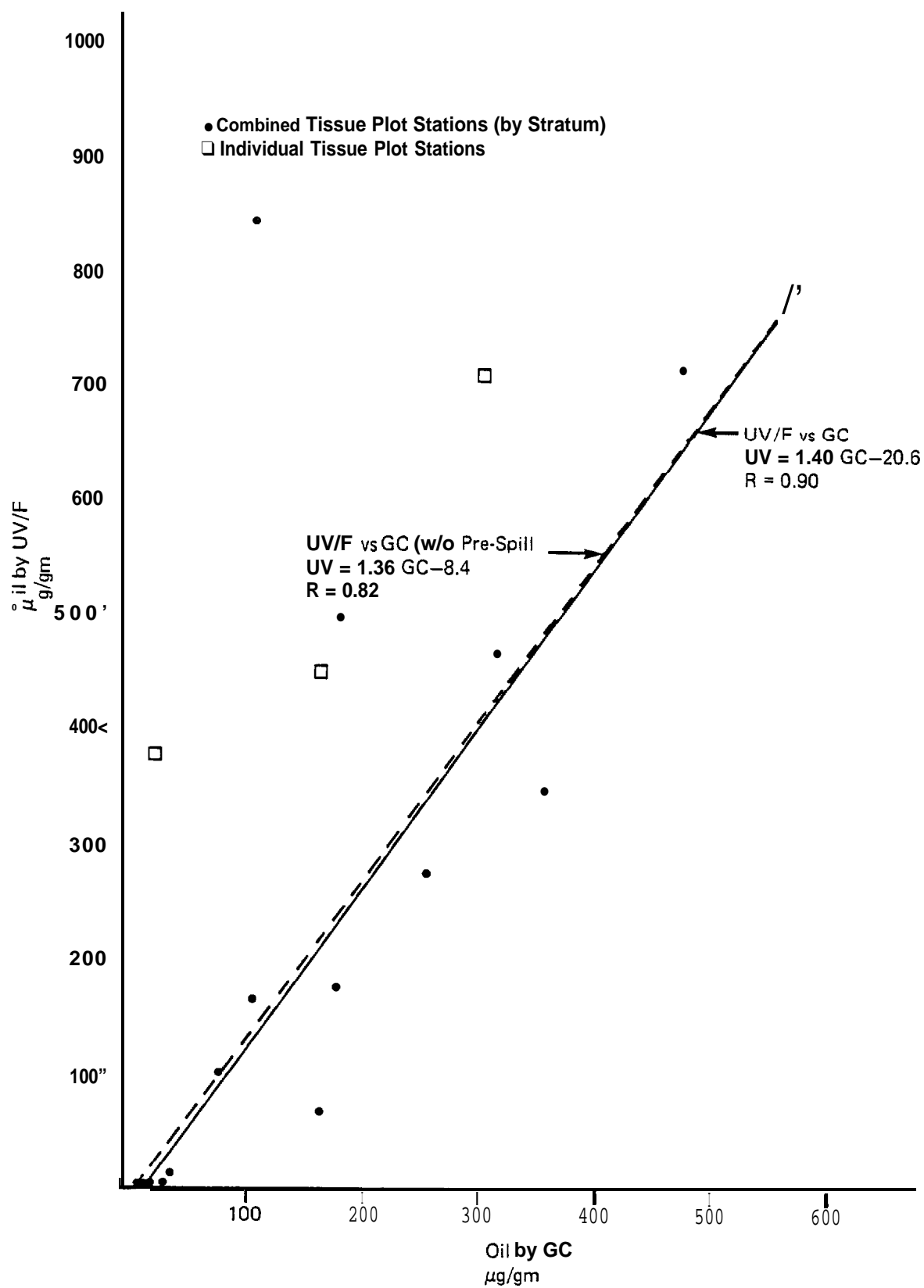
Figure 3.101, Regression of *Serripes* UV/F vs GC^2 Data.

The GC^2 results indicate that there is little compositional variation between the guts: PRIS/PHY = 2.5; ALK/ISO = 1.6; CPI $=$ 1.0, and the muscle: PRIS/PHY = 1.6; ALK/ISO $=$ 2.2; CPI = 1.0. The difference in the ALK/ISO ratio may be significant in that microbial degradation as reflected in the decreasing value for the ratio does occur over time. The gut may be the primary site of the degradation. This is not unexpected for a sample taken one day after the spill. A two-week sample was not available for this type of dissection and analysis, but might have been more instructive vis-a-vis eventual site of petroleum storage. Nevertheless, the one-day sample did show that 69 μg of oil were found per gram (dry weight) in the muscle and 1520 μg of oil were found in the gut. This converts to 300 μg oil per clam in the gut and 65 μg oil per clam in the muscle or 82 percent in the gut.

There was significant variation in the detailed aromatic hydrocarbon patterns (Figure 3.102) of the two parts of the animals on a nanogram per animal basis (i.e. , nanogram per dry weight of total tissue). Figure 3.102 shows that the muscle tissue contained equal or greater quantities of the lower molecular weight compounds (ie., alkyl benzenes and naphthalenes) than did the gut, implying more rapid inward transfer within the animals of these compounds. The alkylated phenanthrene and dibenzothiophenes are twice as abundant in the gut as in the muscle tissue. Note that the unsubstituted phenanthrene and dibenzothiophene compounds are equally proportioned between both tissues, acting more similar to the naphthalenes. The polynuclear aromatics (greater than three rings) reside in the gut to a greater exent than in the muscle. These results imply that the short-term transport of aromatic hydrocarbons within the organism favors the more soluble compounds, while the bulk of the hydrocarbons
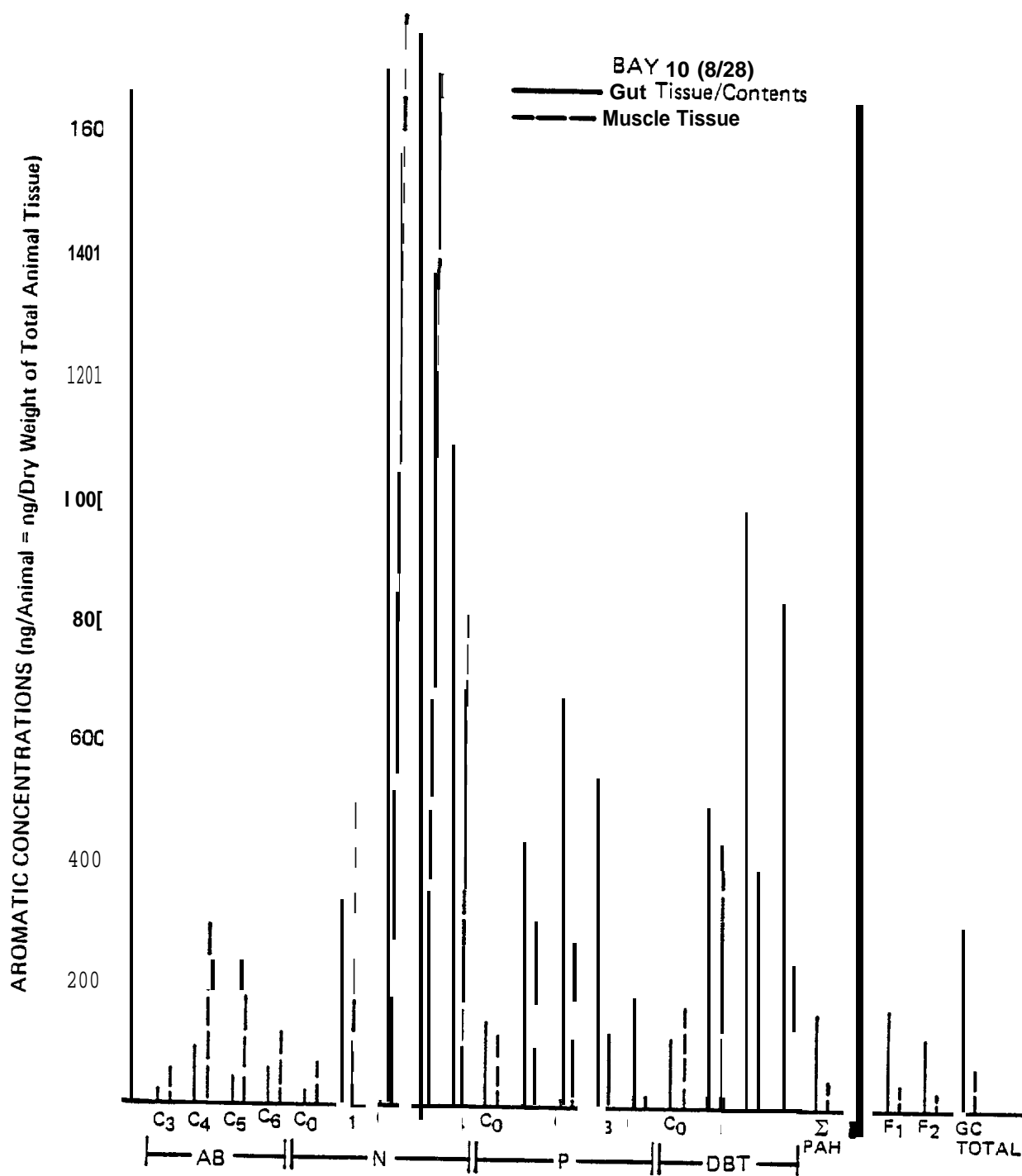
Figure 3.102. Aromatic Hydrocarbon Profiles of *Serripes* Parts.

(saturates and aromatics), ∿82 percent, are mainly present in the gut in the first day following the spill.

It seems paradoxical that these compounds seen to be preferentially incorporated in the muscle tissue in the short term are precisely those compounds most readily lost between the first and second **postspill** periods.

3.4.3 <u>Macoma calcarea</u>

A total of 57 UV/F analyses were performed on **Macoma** 15 GC^2 analyses including transect **poolings** and individual tissue plot station replicates, and 6 GC^2/MS analyses.

3.4.3.1 <u>Bay 9</u>

3.4.3.1a <u>Oil Concentrations by UV/F</u>

<u>Macoma</u> **bivalves display different** trends in oil accumulation than either <u>Mya truncata</u> or <u>Serripes groenlandicus</u>. Results from Bay 9 demonstrate this difference. Concentrations of oil at the time of the **prespill** sampling were 0.73 (.33, **1.2**) µg/g; first **post-spill**, 75 (36, 150) µg/g and second post-spill 836 (610, 1140) µg/g. This pattern, i.e., low initial uptake followed by longer term acquisition of oil, is found in all bays for this species of clam. One possible explanation is a difference in feeding mechanisms between <u>Mya</u> and <u>Serripes</u> (filter feeders) and <u>Macoma</u>, a deposit feeder. Various species of clams may also respond to the initial shock of oil differently; perhaps <u>Macoma</u> slows its pumping considerably in the presence of a large water column loading of oil and discontinues feeding for a period of

time, whereas the _Mya_ clam is not as sensitive, continues
feeding, and hence acquires high levels of oil by the first
pre-spill sampling (see Figures 3-103 and 3-104).

3.4.3.1b Oil Composition by GC[2]

The pre-spill samples are devoid of any traces of petro-
leum as was also the case for other species. The f2 fraction
does, however, contain an assemblage of olefinic clusters
which are a unique characteristic of this species of deposit
feeder. The presence of these olefins (also found in surface
sediments) obscures the phenanthrene/dibenzothiophene region
of the GC^2 trace so GC^2/MS (see next section) is required
to examine the aromatic distributions. That these organisms
feed on surface detritus is confirmed by these olefins and
by the odd-chain predominance of alkanes in the C_{25}-C_{31} region
as measured by the carbon preference index (CPI) in prespill
Macoma ($\sim$3.0). As oil is ingested, the CPI approaches that
for oil (i.e., 1.0) but never loses a slight odd carbon
preference (CPI = 1.1-1.3).

In the first post-spill sampling (August 28), oil is
detected in the _Macoma_ tissues, but at low levels. Note
though that an odd/even predominance still exists in the
one-day saturate fraction (CPI=1.3). At two weeks the CPI
equals 1.0 and the GC^2 saturate trace reflects the presence
of a large amount of oil (650 ppm).

The ratio of n-C_{18} to phytane (18/phy) can be used as
a biodegration indicator rather than the ALK/ISO due to the
large natural abundance of pristane in the _Macoma_ samples.
Between the initial oiling and the two-week sampling time
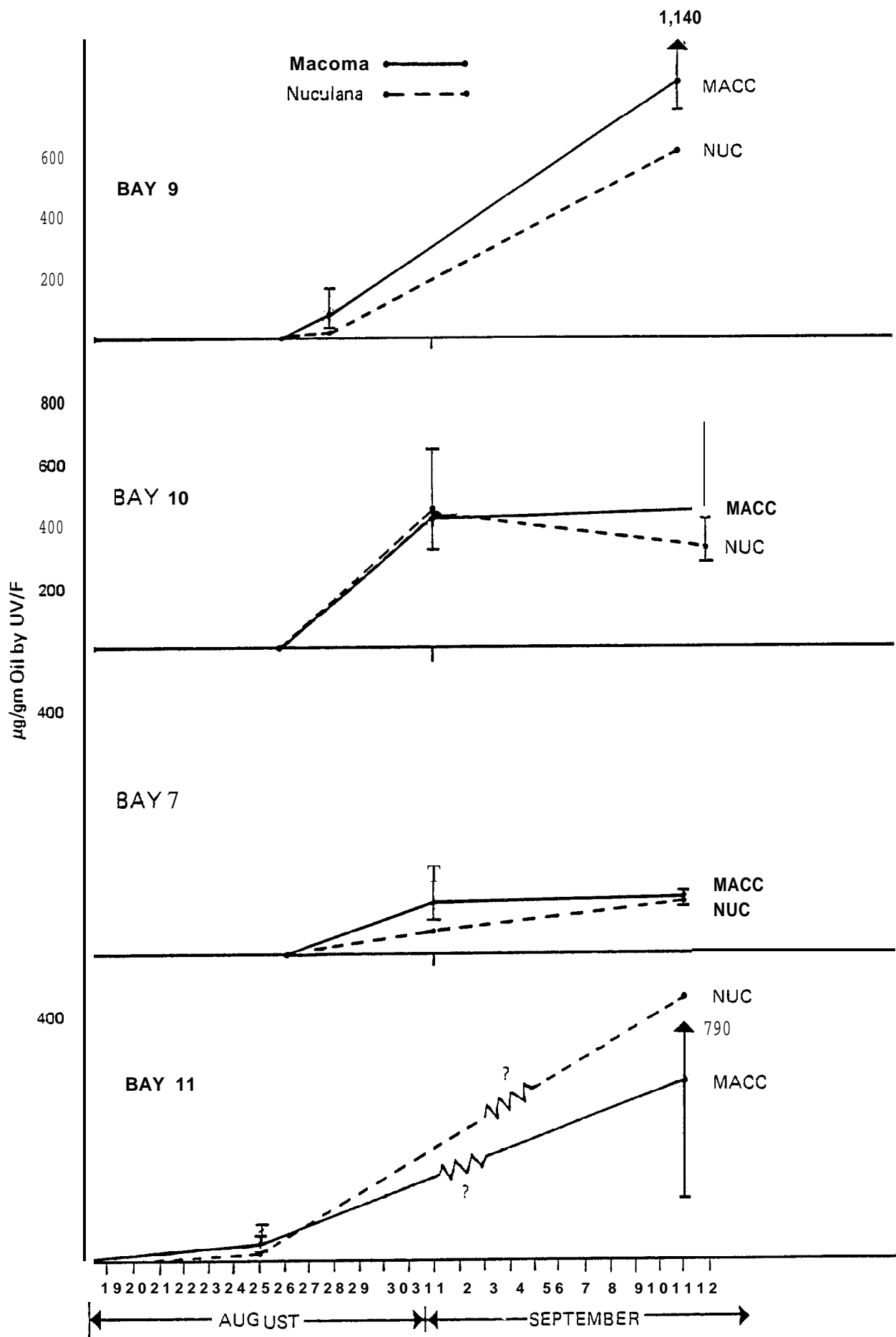
Figure 3.103. Trends in __Macoma__ and __Nuculana__ Concentrations by UV/F.

TISSUE
PLOTS
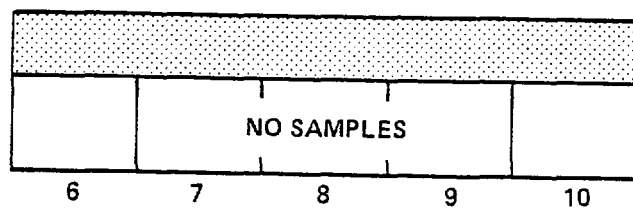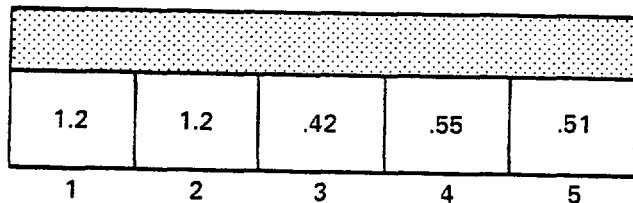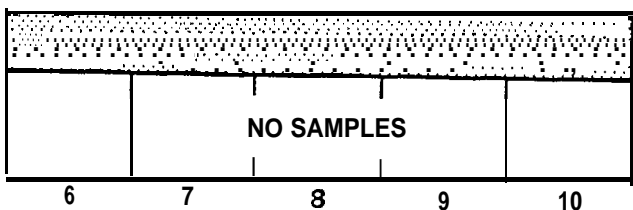
PRESPILL
8 AUG 81

NO SAMPLES   3m

6   7   8   9   10

1.2   1.2   .42   .55   .51   7m   .73 (.33, 1.2)*

1   2   3   4   5

FIRST POSTSPILL
28 AUG 81

NO SAMPLES   3m

6   7   8   9   10

73.   31.   64.   136.   117.   7m   75. (36, 150)

1   2   3   4   5

SECOND POSTSPILL
11 SEP 81

NO SAMPLES   3m

6   7   8   9   10

586.   727.   1010.   883.   1093.   7m   836. (610, 1,140)

1   2   3   4   5
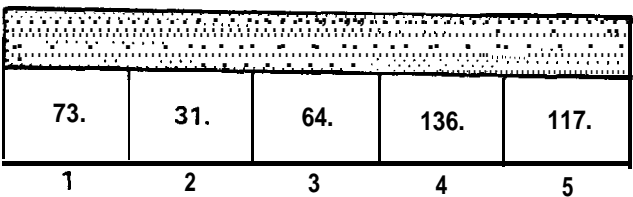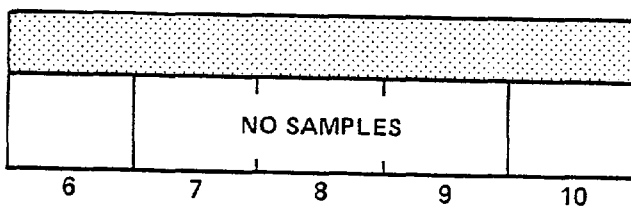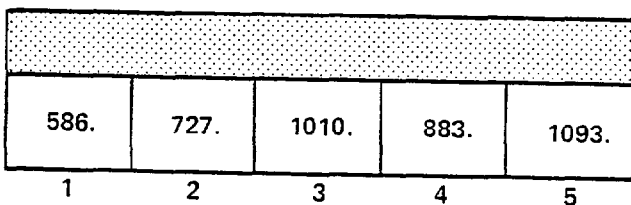
*95% Confidence Limits

Figure 3.104. Concentrations of Oil in Macoma calcarea, Bay 9 by UV/F (μg/g).

only a modest reduction in the 18/phy ratio is noted (1.7 to 0.83). This contrasts with <u>Mya</u> and <u>Serripes</u> results which illustrated a significant <u>in vivo</u> degradation of the n-alkanes of assimilated oil in the one-day to two-week interval. The lesser importance of this apparent degradation in <u>Macoma</u> could very well be a result of a continual uptake of oil from the sediment after an initial water column impact, or to lack of the required microfloral population in the gut of the animal.

The f2 GC^2 traces continue to be dominated by the olefinic clusters through the two-week sampling, but the appearance of a broad range of aromatic hydrocarbons does become evident in the GC^2 trace.

3.4.3.1c <u>Aromatic Hydrocarbon Composition by GC^2/MS</u>

Aromatic hydrocarbon data from GC^2/MS analyses of a one-day and two-week composite samples indicate that there is no basic difference in the aromatic hydrocarbon **assemblage between the two** time periods. A full range of the major **two-** and three-ring aromatic, hydrocarbons, (naphthalenes, phenanthrenes), and the important aromatic heterocyclic series (dibenzothiophenes), were found (Figure 3-105). Concentrations of all aromatics increased between the initial (one-day) and two-week samplings owing to an increase in total oil assimilated. Virtually no compositional changes were observed, with the two-week samples containing sizeable quantities (0.5 ppm) of total naphthalene compounds (C_0-C_4) and much elevated phenanthrene (C_0-C_4)($\sim$2 ppm) and dibenzothiophene (C_0-C_3) (3 ppm) levels.
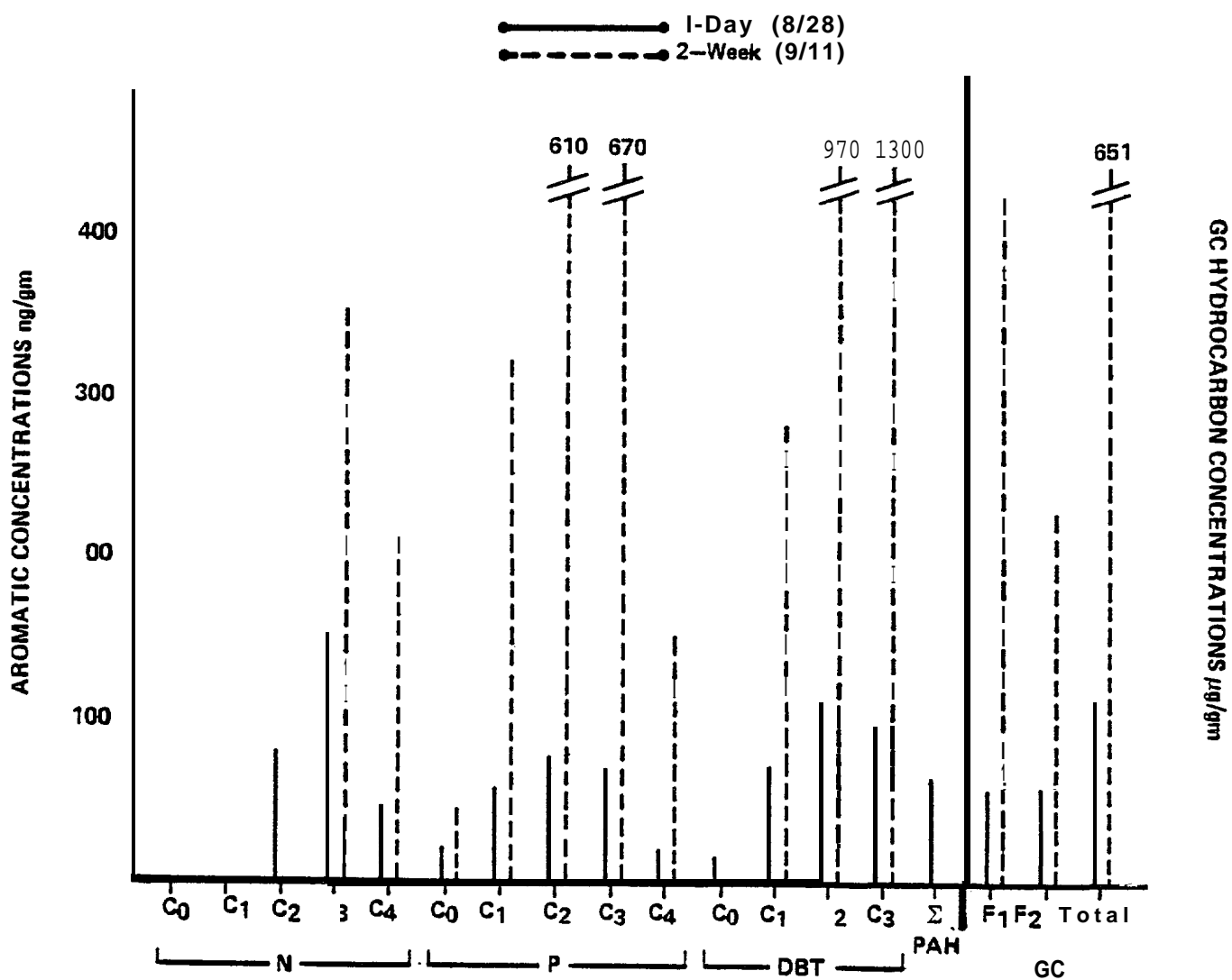
Figure 3.105. Macoma Aromatic Profiles by GC^2/MS (Bay 9).

3.4.3.2 Bay 10

3.4.3.2a Oil Concentrations by UV/F

Bay 10 has consistently contained the highest concentrations of oil in clams compared to the other three bays perhaps due to the timing of the first post-spill sampling. Macoma pre-spill concentrations for this bay were 2.1 (1.0, 3.6) $\mu g/g$; first day post-spill concentrations were higher (406 [241, 6801 $\mu g/g$) than Bay 9 levels, and remained at 440 (250, 760) $\mu g/g$ during the second post-spill sampling (statistically equal to the first postspill). These data still support a different accumulation method for Macoma as opposed to the two earlier species of clams. As the first post-spill sampling at Bay 10 was later than that for Bay 9 it is entirely plausible that the initial concentration differences between Bays 9 and 10 are due to this time difference (see Figures 3-103 and 3-106).

3.4.3.2b Oil Composition by GC^2

GC^2 profiles of the Bay 10 Macoma samples were similar to those from Bay 9. An important exception was the apparent greater extent of biodegradation of the Bay 10 two-week samples compared with the Bay 9 set, reflected by a greater relative importance of the isoprenoids compared to the alkanes (18/phy=0.66). Otherwise, the Bay 9 and 10 GC^2 profiles are very similar, including the CPI values greater than 1, indicating a continued terrigenous biogenic n-alkane influence.

TISSUE
PLOTS
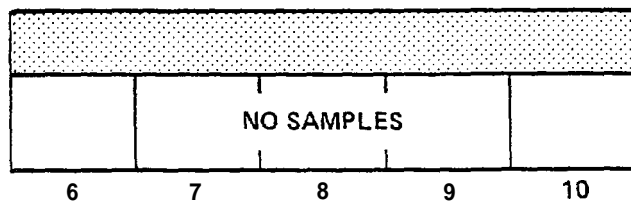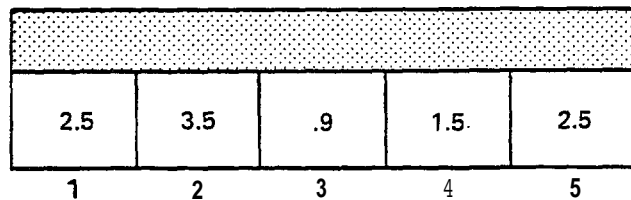
PRESPILL
14 AUG 81

		NO SAMPLES		
6	7	8	9	10

3m

2.5	3.5	.9	1.5.	2.5
1	2	3	4	5

7m

2.1 (1.0, 3.6)*

FIRST POSTSPILL
1 SEP 81

		NO SAMPLES		
6	7	8	9	10

3m

324.	254.	503.	354.	748.
1	2	3	4	5

7m

406. (241 , 680)

SECOND POSTSPI LL
12 SEP 81

		NO SAMPLES		
6	7	8	9	10

3m

427.	581.	450.	676.	—
1	2	3	4	5
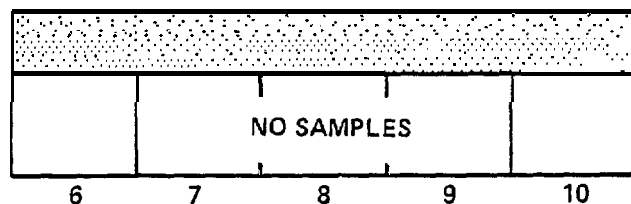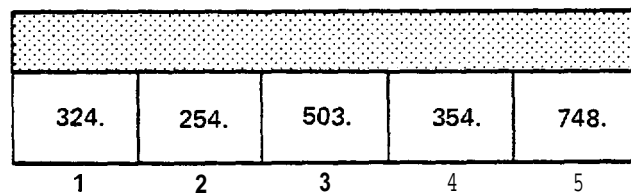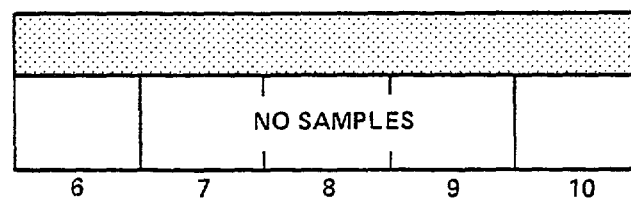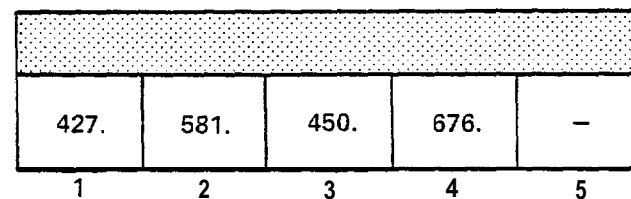
7m

440. (250, 760)

*95% Confidence Limits

Figure 3.106. Concentrations of Oil in Macoma calcarea Bay 10 by UV/F (μg/g).

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3.4.3.3 Bay 7

3.4.3.3a Oil Concentrations by UV/F

Pre-spill clams contained 1.0 (.88, 1.2) $\mu g/g$ "oil equivalents"; first post-spill clams oil concentrations rose to 82 (60, 112) $\mu g/g$; and second post-spill clams contained the statistically equivalent 86 (39, 190) $\mu g/g$ oil. This pattern is again typical of the Macoma clam, except at much lower levels than observed in Bays 9 or 10. The lack of increase of oil in Bay 7 animals beyond ~ 60 ppm is probably due to a lack of sediment contamination in Bay 7 (see Figure 3-103 and 3-107), and suggests then, that the levels of oil found in Bays 9 and 10 reflect a continued accumulation of oil from sediments in Bays 9 and 10.

3.4.3.3b Oil Composition by GC^2

Levels of assimilated hydrocarbons were lower at Bay 7 than at Bay 9 or 10 during both sampling periods. The one-day (actually five days post-spill) GC^2 profiles indicated that Macoma from Bay 7 did acquire low levels of undegraded oil, and show a distinct odd/even preference (CPI=1.3). The aromatic hydrocarbon GC^2 profiles continued to be totally dominated by the olefinic clusters. The two-week (September 11) sample illustrated marked biodegradation and weathering of the acquired oil (18/phy=0.4) and no change in CPI between September 1 - 11, indicating that Bay 7 Macoma were no longer acquiring additional oil, unlike the Bay 9 and 10 situations.

**TISSUE
PLOTS**

		NO SAMPLES			3m
6	7	8	9	10	

.92	1.2	.91	1.1	1.2	7m
1	2	3	4	5	

1. (.88, 1.2)*

FIRST POSTSPILL
1 SEP 81

		NO SAMPLES			3m
6	7	8	9	10	

94.	58.	92.	69.	107.	7m
1	2	3	4	5	
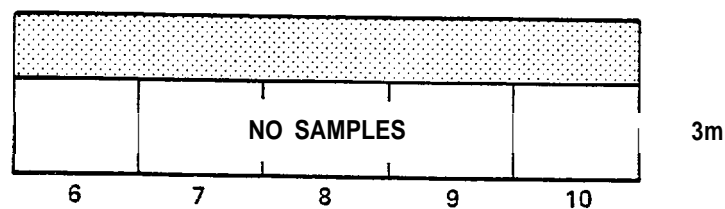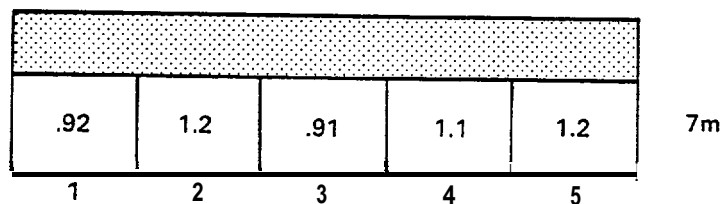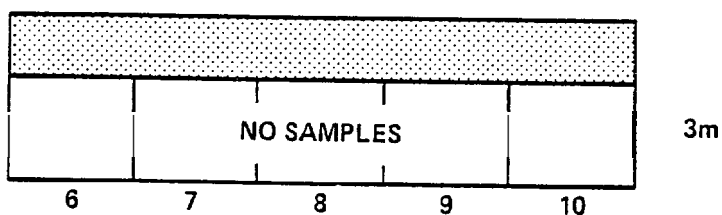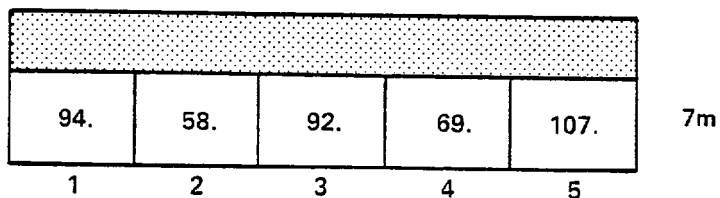
82. (60, 112)

SECOND POSTSPILL
11 SEP 81

		NO SAMPLES			3m
6	7	8	9	10	

28.	102.	104.	131.	115.	7m
1	2	3	4	5	
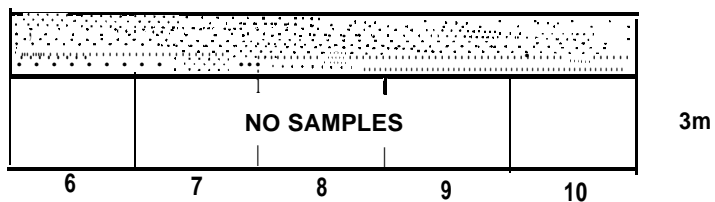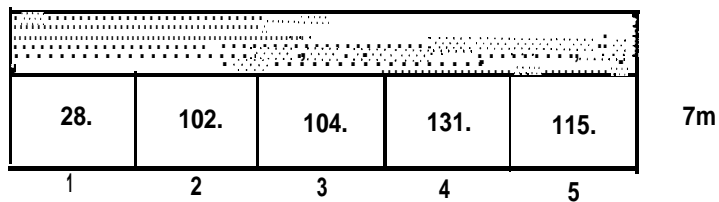
85. (39, 190)

*95% Confidence Limits

Figure 3.107. Concentrations of oil in Macoma calcarea, **Bay 7 by UV/F** (μg/g).

3.4.3.3c Aromatic Hydrocarbon Composition by GC^2/MS

The GC^2/MS analytical results for aromatic hydro-
carbons in Bay 7 Macoma (Figure 3-108) indicate that only
small quantities of a highly weathered aromatic **assemblage**
(i.e., predominantly highly **alkylated** phenanthrenes and
dibenzothiophenes) are detected only in the two-week samples.
Less than 100 ppb of phenanthrenes and less than 50 ppb of
dibenzothiophenes are detected in these samples, a much
smaller chemical impact than that observed at any of the other
bays.

3.4.3.4 Bay 11

3.4.3.4a Oil Concentrations by UV/F

Pre-spill oil concentrations found in Macoma were
2.5 (.05, 10) µg/g; first post-spill concentrations avera9ed
24 (14, 42) µg/g and second post-spill concentrations increased
to 246 (76, 790) µg/g oil in the clams.   The high second
post-spill concentrations probably reflect both the delayed
influx of oil to the Bay 11 **benthos** and Macoma's oil accumu-
lation patterns (i.e., slow initial uptake followed by increased
oil accumulation with time).   The first post-spill increase in
oil (and in Nuculana; see next Section 3.4.4) closely reflects
the post-surface spill (Bay 11) pre-dispersed oil spill
(Bays 9 and 10) **benthic** impact at Bay 11 (see Figure 3-103
and 3-109).
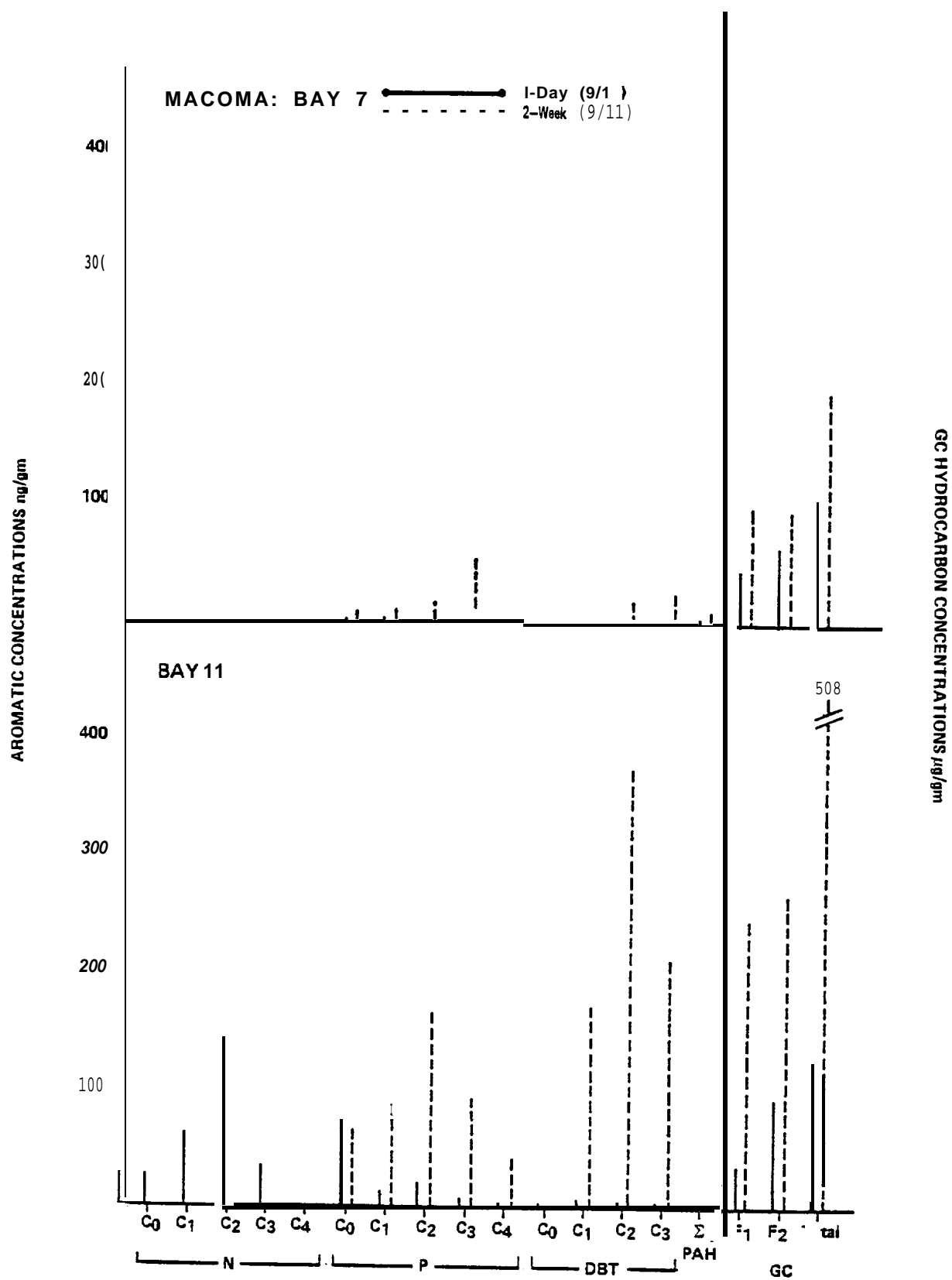
Figure 3.108. Aromatic hydrocarbon profiles in Macoma by GC²/MS (Bay 7 and 11.)

PRESPILL
13 AUG 81

NO SAMPLES   3m

6   7   8   9   10

| — | 2.1 | 2.5 | 8.1 | .5 |

1   2   3   4   5

7m   2.5 (.05, 10)*

FIRST POSTSPILL
25 AUG 81

NO SAMPLES   3m

6   7   8   9   10

| 21. | 24. | 26. | 14. | 46. |

1   2   3   4   5
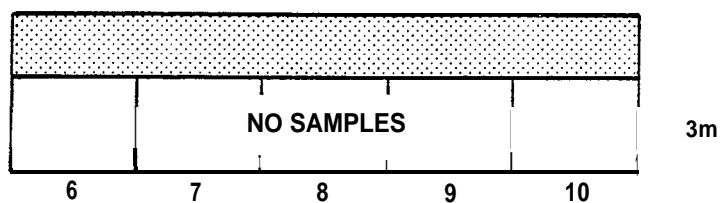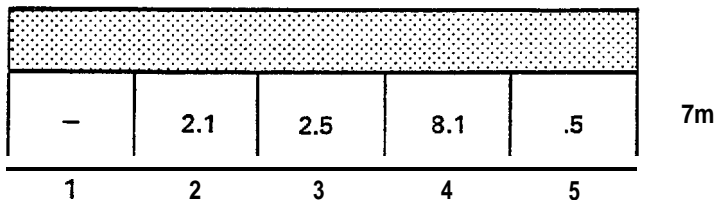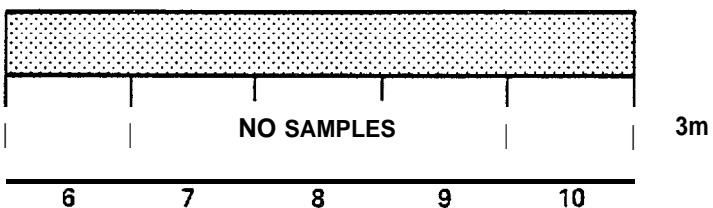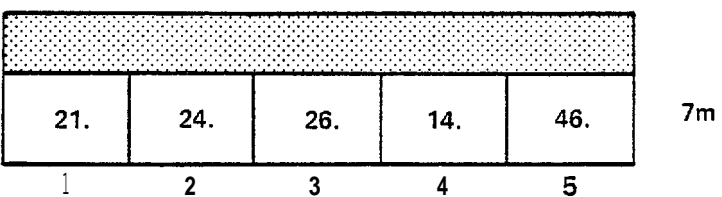
7m   24. (14, 42)

SECOND POSTS?! LL
11 SEP 81

NO SAMPLES   3m

6   7   8   9   10

| 99. | 186. | 401. | 491. | — |

1   2   3   4   5
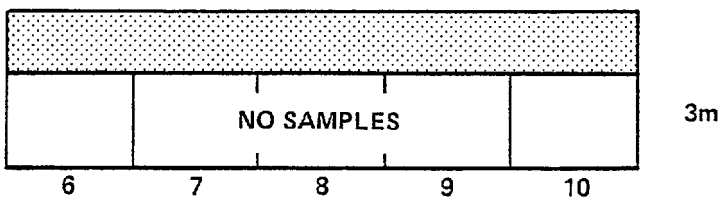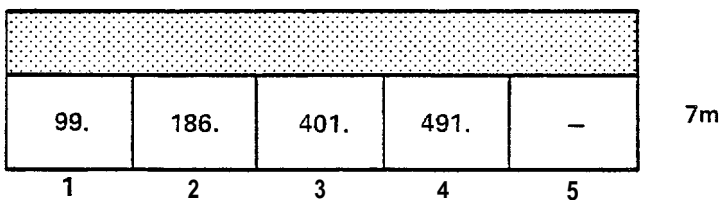
7m   246. (76, 790)

*95% Confidence Limits

Figure 3.109. Concentrations of oil in Macoma calcarea, Bay 11 by UV/F (μg/g).

-266-

3.4.3.4b Oil **Compositions by** GC^2

No detectable petroleum components were found by GC^2
in the "one-day" (actually two-day; September 21) samples from
Bay 11, the GC^2 profiles reflecting the purely biogenic
inputs in both the f_1 and f2 fractions (CPI=1.94). Oil
was detected in the "two-week" (September 11=3 week) samples,
yielding a GC^2 profile almost identical to two-week samples
observed in the other bays. The two-week CPI reflected this
petroleum input (=1.00) as did the large abundance of normal
and branched alkanes.

3.4.3.4c Aromatic Hydrocarbon Composition by GC^2/MS

Detailed scrutiny of the Bay 11 aromatics indicated some
unique trends (Figure 3-108). First, although whole oil was
not detected in the initial (two-day) samples, the presence of
the naphthalene series and phenanthrene itself indicate that
prior to whole oil uptake by Macoma in Bay 11, the water-
soluble aromatics were introduced to the benthic system and
were acquired by Macoma at a **250** ppb (total naphthalene) level
prior to the dispersed oil spill in Bay **9.** Subsequently, the
oil impact at Bay 11 from beach erosion is revealed through
the high abundance of the phenanthrene and dibenzothiophene
compound series (~550 and 700 ppb, respectively). Note that
the two-week samples do not contain any naphthalenes while the
one-day samples contain no dibenzothiophenes. Thus, the
aromatic compositions reflect a change in the nature of the
petroleum components available to the Bay 11 benthos during
the three week post-spill period.

3. 4.3.5 UV/F VS. GC[2] Analysis

Linear regression analysis of Macoma UV/F weighted averages versus GC2 strata data is similar to Serripes, Figure 3.110. The large y-intercept of -100.3 reflects the biogenic assemblages measured in the resolved f2 GC2 fraction, which are not seen by UV/F. Indeed, if UV/F data is compared to the f_1 + unresolved f2 GC2 values, the slope remains essentially the same (1.34) and the y-intercept increases to 54.0, reflecting the drop in background.

3.4.4 Astarte borealis

3.4.4.1 Bav 9

3.4.4.1a Oil Concentrations by UV/F

UV/F data (Figures 3-111 and 3-112) indicate that the same pattern found earlier with Mya and Serripes is also characteristic of the Astarte clams. Pre-spill concentrations were 0.81 (.44, 1.3) µg/g; first postspill concentrations increased to 463 (270, 800) µg/g, similar to the Serripes results from Transect 1. The second post-spill concentrations dropped to 171 (88, 330) µg/g of oil.

3.4.4.1.b Oil Composition by GC[2]

GC[2] profiles of Astarte from Bay 9 show that after initial accumulation of moderately weathered oil (Figure 3.113), microbial degradation proceeds very rapidly, resulting in a near total depletion of n-alkanes less than
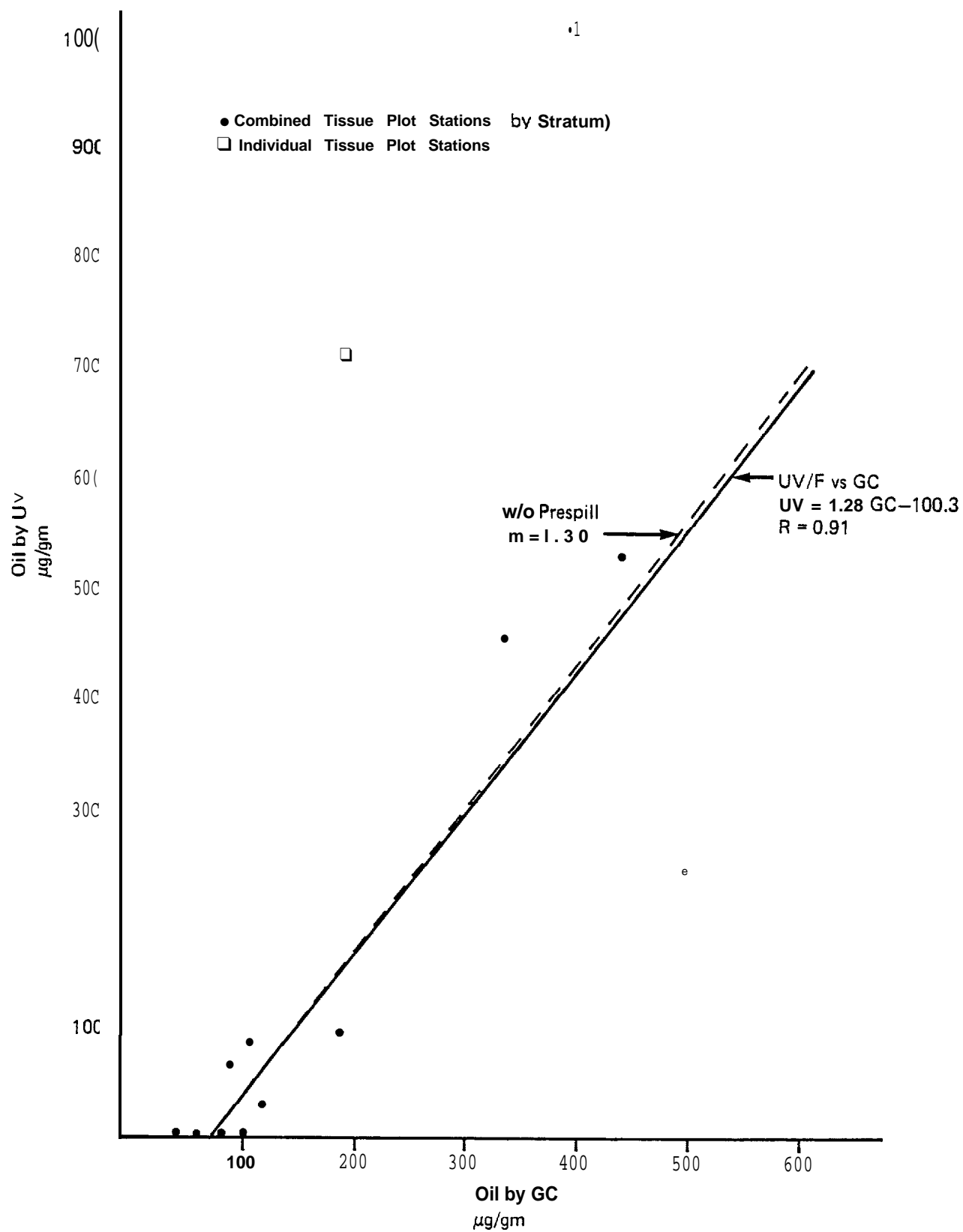
Figure 3.110. Regression of *Macoma* UV/F vs GC2 Data.
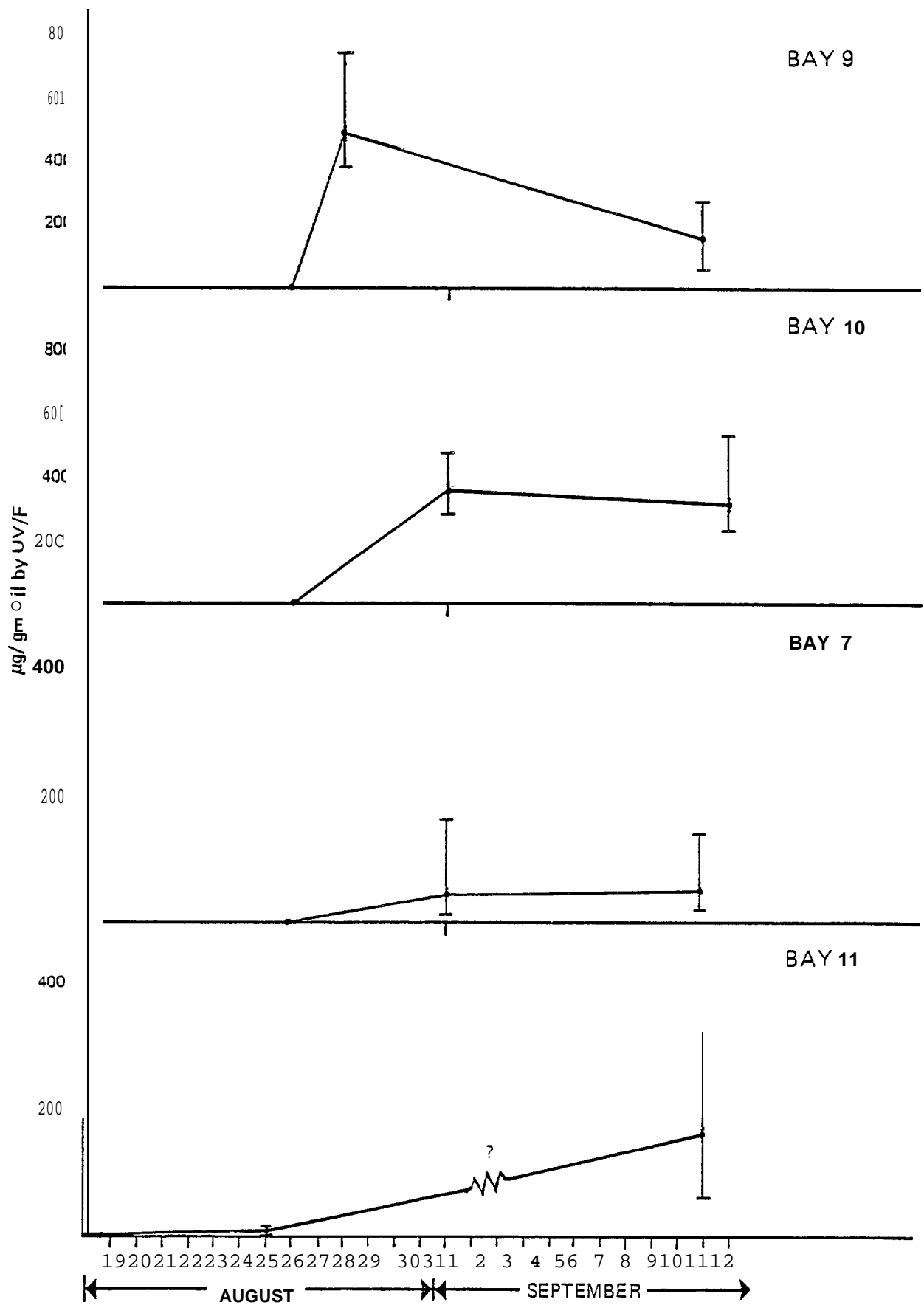
Figure 3.111. Trends in oil concentrations in _Astarte_ by UV/F.

TISSUE PLOTS

PRESPILL
8 AUG 81

NO SAMPLES — 3m

| 6 | 7 | 8 | 9 | 10 |

| – | .46 | .91 | .95 | .98 | 7m
| 1 | 2 | 3 | 4 | 5 |

.81 (.44, 1.3)*

FIRST POSTSPILL
28 AUG 81

NO SAMPLES — 3m

| 6 | 7 | 8 | 9 | 10 |

| 365. | 386. | 898. | 289. | 570. | 7m
| 1 | 2 | 3 | 4 | 5 |
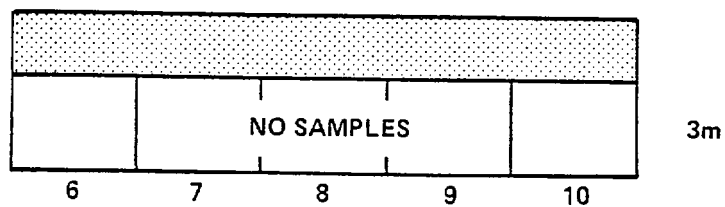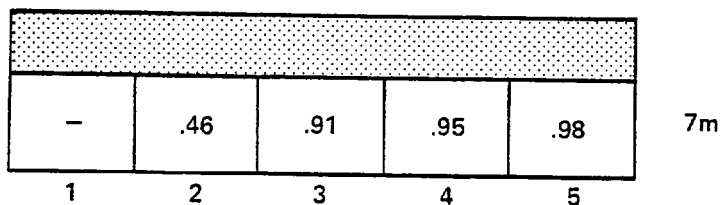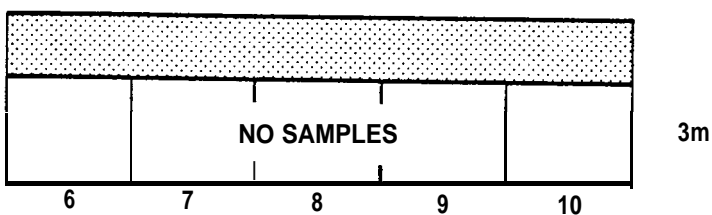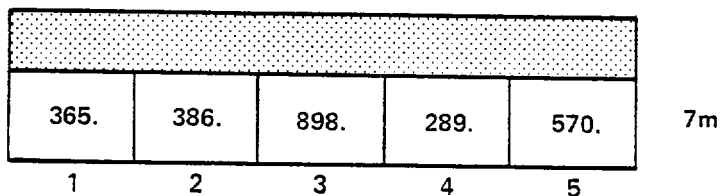
463. (270, 800)

SECOND POSTSPILL
11 SEP 81

NO SAMPLES — 3m

| 6 | 7 | 8 | 9 | 10 |

| 297. | 98. | 298. | 108. | 155. | 7m
| 1 | 2 | 3 | 4 | 5 |
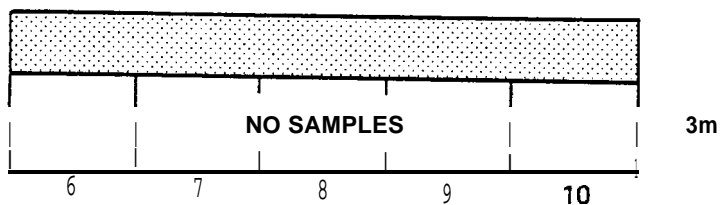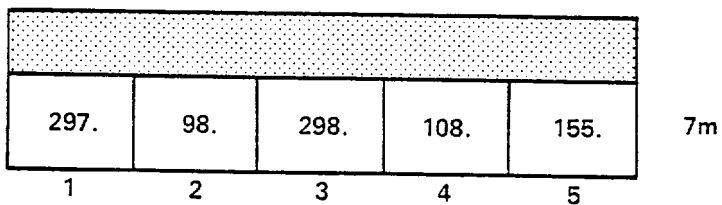
171. (88, 330)

*95% Confidence Limits

Figure 3.112. Concentrations **of oil in Astarte borealis, Bay 9 by UV/F** (μg/g).

-271-

Figure 3.113. Saturated Hydrocarbon GC^2 profiles of *Astarte* sample from Bay 9.
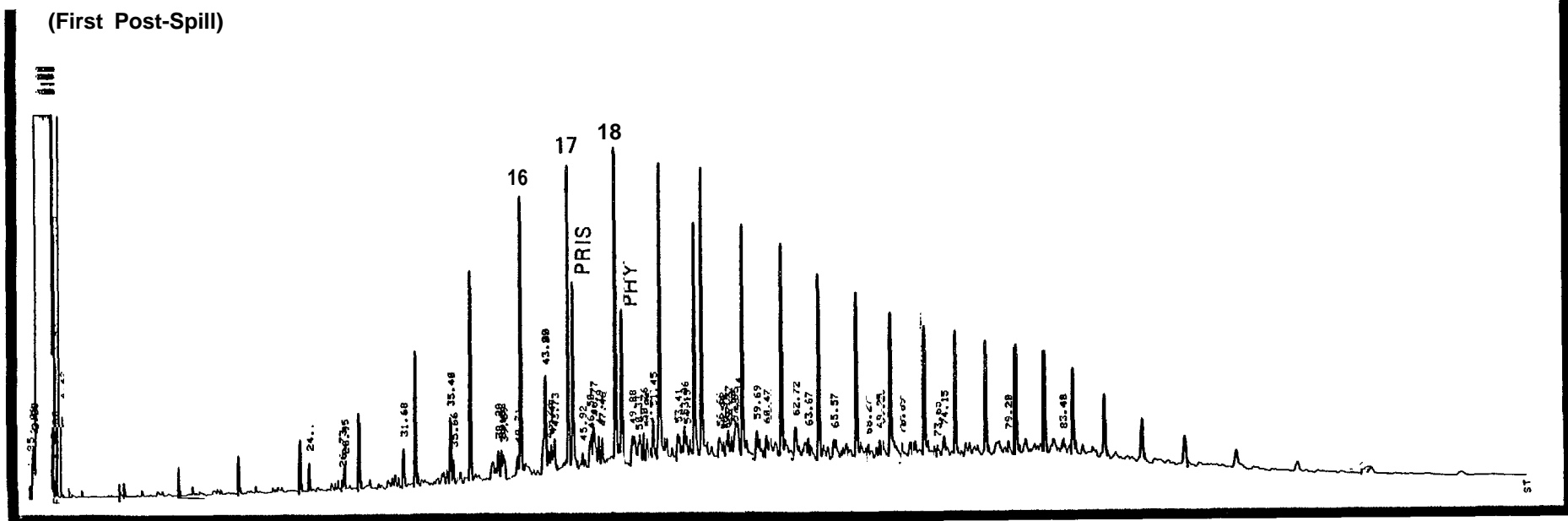
$n-C_{20}$ and a resultant change in the ALK/ISO ratio from
2.0 to 0.15 (i.e., the preferential loss of n-alkanes versus
isoprenoids). Initially, the saturated hydrocarbon concen-
tration represented 78 percent of the total accumulated oil.
This percentage decreased ,presumably due in a large part to
in vivo microbially mediated degradation, to approximately
50 percent in the second post-spill sampling. The oil
initially taken up by Bay 9 Astarte appears to be depleted
in the lower molecular weight alkanes ($<n-C_{14}$) relative to
the oil acquired by Bay 9 Mya and Serripes, the latter oil
considerably "richer" in the $n-C_9$ to $n-C_{14}$ (see Figures 3.75
and 3.90). Furthermore, the aromatic profiles (Figure 3.114)
indicate that the oil accumulated initially by Astarte is
also depleted in light aromatics compared with Mya and
Serripes (see Figure 3.76).

A significant assemblage of $n-C_{20}$ to $n-C_{30}$ n-alkanes
persist in the Astarte tissues much like Serripes, but unlike
Mya.

3.4.4.1.c Aromatic Hydrocarbon Composition by GC^2/MS

Two sample composites were analyzed for their detailed
aromatic hydrocarbon profiles (Figure 3.115). Results from
the first post-spill sample indicate that in the first day
following the spill significant quantities of naphthalenes
are accumulated along with the other aromatic families. In
the two weeks following this initial sampling, naphthalene
levels decrease yet phenanthrene and dibenzothiophene series
levels remain relatively constant. After two weeks, the
concentration of phenanthrenes is roughly equal to 2.9 ppm,
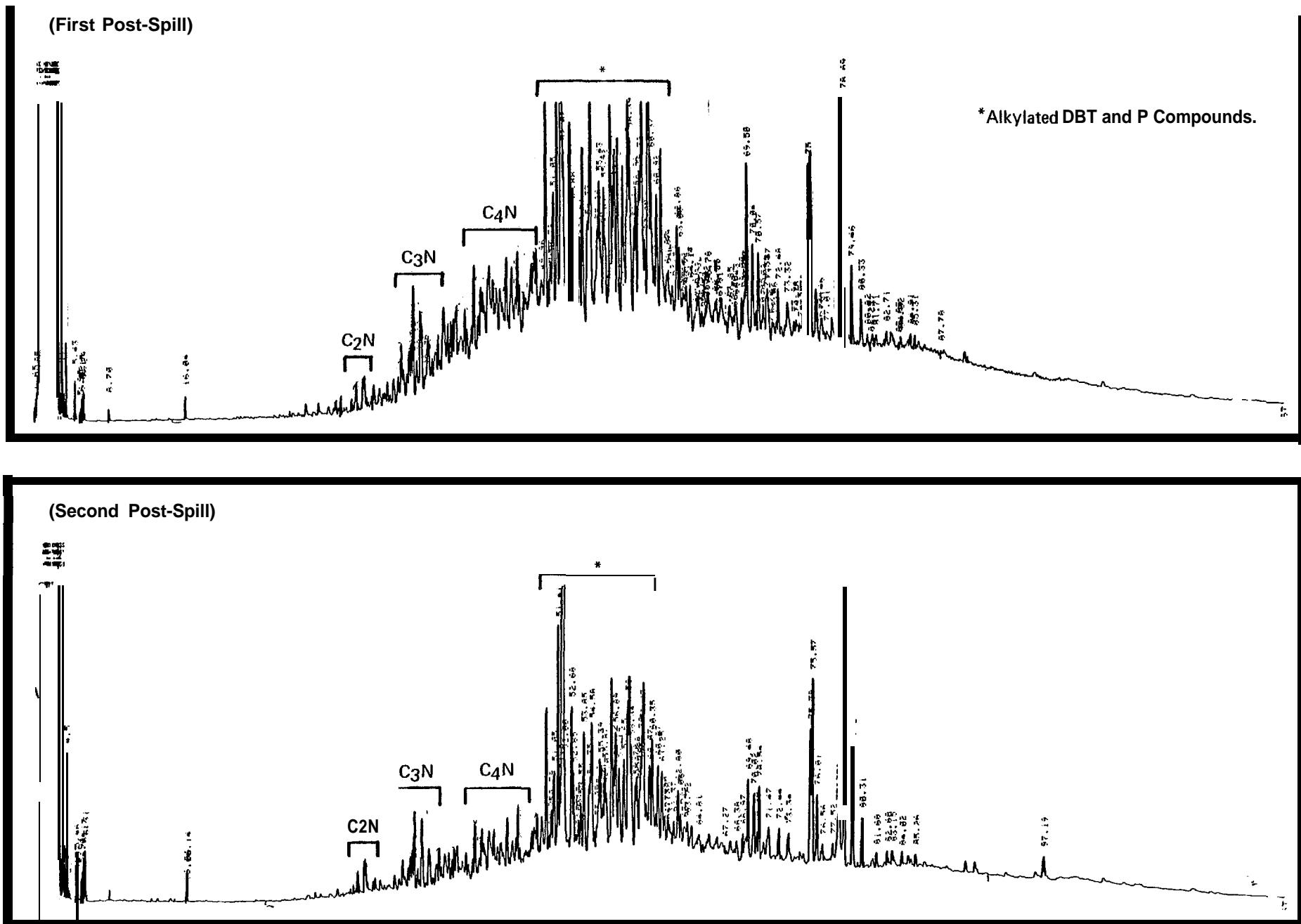
Figure 3.114. Aromatic Hydrocarbon GC^2 profiles of *Astarte* sample composite from Bay 9.
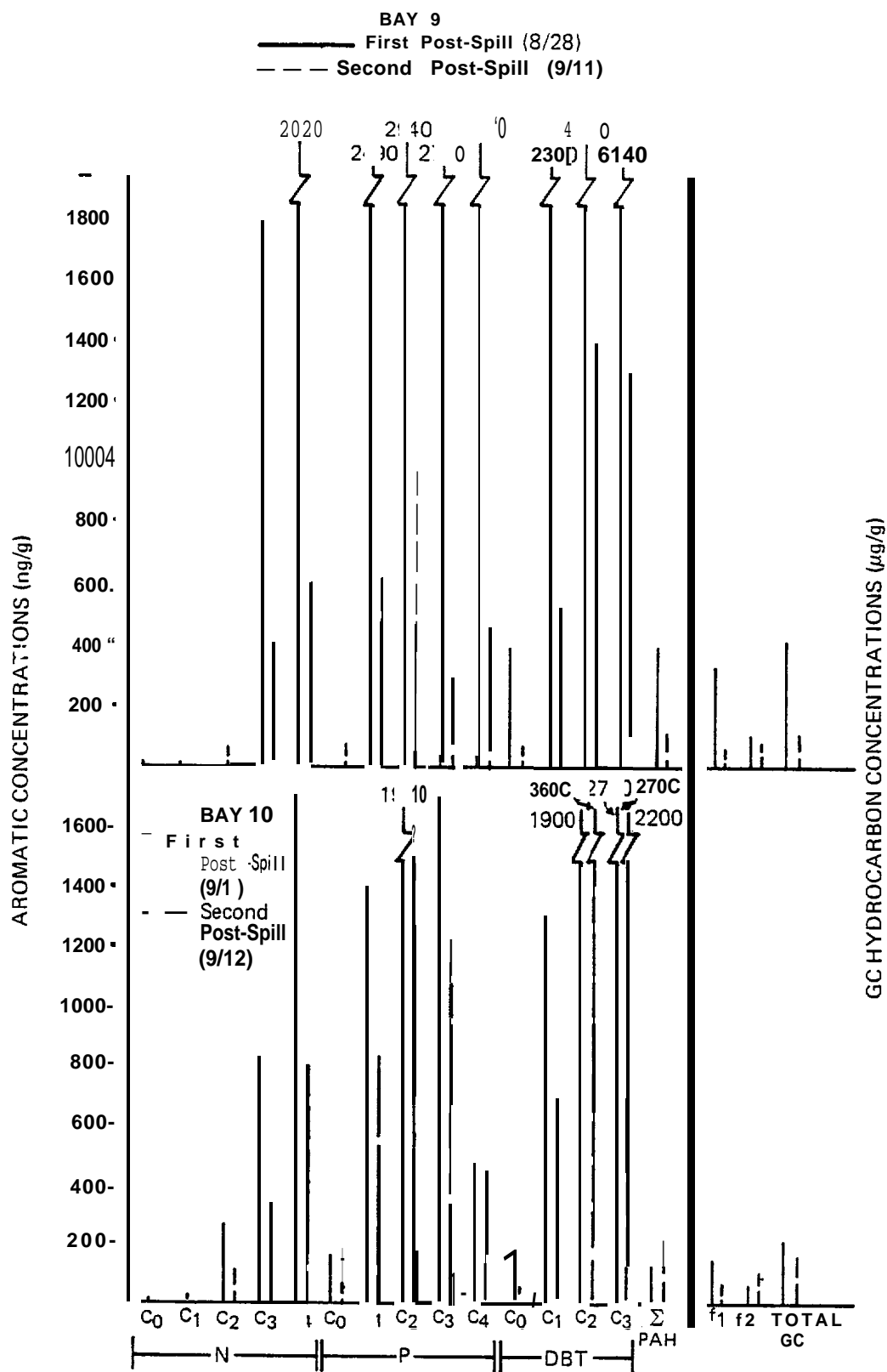
Figure 3.115. _Astarte_ Aromatic Profiles (Bays 9 and 10).

dibenzothiophenes equal to 3.3 ppm, and **naphthalenes** equal
to 1 ppm. These levels are higher than those in either <u>Mya</u>
or <u>Serripes,</u> although on a gross **basis,** oil levels in
<u>Serripes</u> and <u>Astarte</u> are similar during both sampling
periods. Thus, <u>Astarte</u> behaves much like <u>Serripes</u> vis-a-vis
extended retention of phenanthrene and dibenzotiophene
compounds in spite of significant **naphthalene** and gross oil
level deputation.

3.4.4.2 **B a y 1 0**

3.4.4.2a <u>Oil Concentrations by UV/F</u>

Oil equivalents concentrations in <u>Astarte</u> for **pre-spill**
samples are predictably low 0.43 (.25, .64) µg/g. The first
post-spill concentrations are again similar to <u>Serripes,</u>
364 (320, 410) µg/g, and second post-spill decreased only
slightly to 310 (210, 460) µg/g oil. <u>Astarte</u> clams in this
bay did not appear to clear oil from tissue as readily as
<u>Astarte in</u> Bay 9, *or* <u>Mya</u> or <u>Serripes clams</u> in Bay 10 (see
Figure 3-111 and 3-116).

3.4.4.2b <u>Oil Composition by GC</u>^{2}

GC^2 results for Bay 10 are similar to the Bay 9 compo-
sitional results with two exceptions. Firstly, although
the degradation of **n-alkanes** is again apparent, the rate of
degradation in Bay 10 animals appears greater. The ALK/ISO
ratio in the first post-spill (September 1) Bay 10 animals
was 1.3 compared with 2.0 for Bay 9, thus indicating the
advanced state of degradation in Bay 10 animals. The second
post-spill (September 11) **ALK/ISO** ratio was 0.13, quite

TISSUE PLOTS
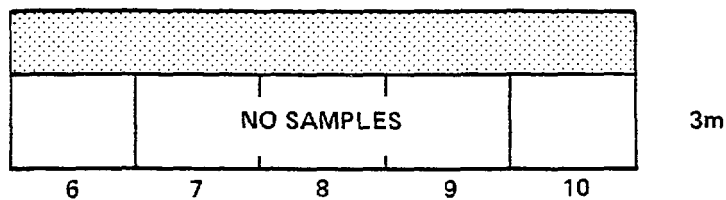
	NO SAMPLES				3m
6	7	8	9	10	

PRESPILL
14 AUG 81

.29	.31	.37	.57	.64	7m
1	2	3	4	5	

.43 (.25 , .64)*

	NO SAMPLES				3m
6	7	8	9	10	

FIRST POSTSPILL
1 SEP 81

353.	340.	358.	—	407.	7m
1	2	3	4	5	

364. (320, 410)

	NO SAMPLES				3m
6	7	8	9	10	

SECOND POSTSPILL
12 SEP 81

377.	177.	385.	338.	325.	7m
1	2	3	4	5	
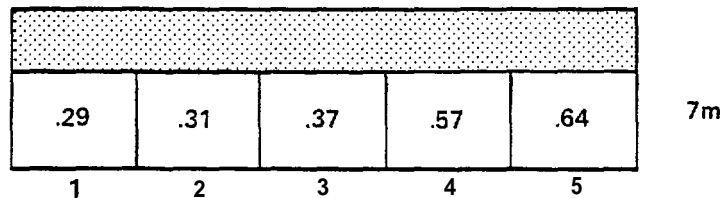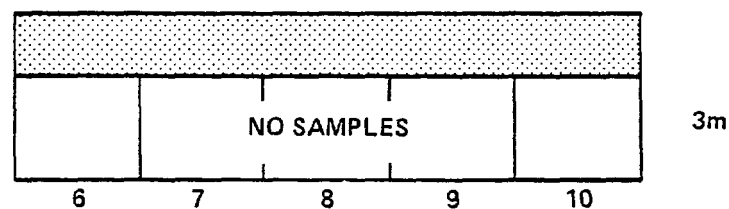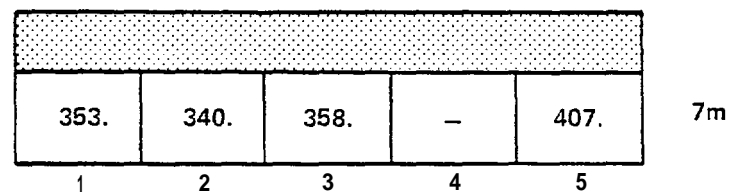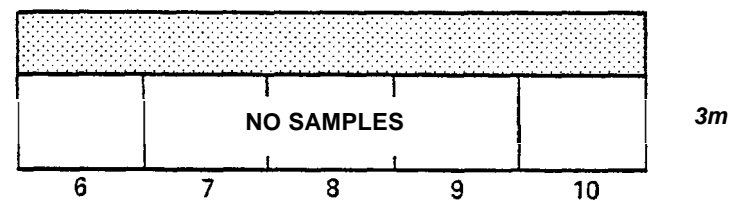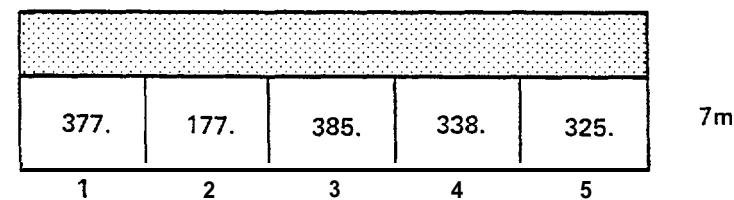
310. (210, 460)

'95% Confidence Limits

Figure 3.116. Concentrations of oil in Astarte borealis, Bay 10 by UV/F (#g/g).

similar to the Bay *9* result.   This difference in Bay 9 and 10 animals is probably due to the fact that Bay 10 animals were sampled 4 days after the spill, while Bay 9 was sampled one day after.   Thus, we see degradation proceeding during the first several days, being nearly complete (i.e., loss of n-alkanes less than $n-C_{20}$) in two weeks.   As in Bay 9, the $n-C_{21}$ to $n-C_{34}$ alkanes persist as a distinct chromatographic feature.

Secondly, while Bay 9 concentrations decreased with time, the Bay 10 GC^2-determined overall concentration of oil remained elevated over two weeks.   Over time, the pristane/phytane ratio increased in both Bay 9 and 10, owing presumably to inputs of biogenic pristane rather than to preferential degradation of phytane.

3.4.4.2c Aromatic   Hydrocarbon   Composition   by GC^2/MS

The Bay 10 aromatic hydrocarbon determinations (Figure 3.115) again indicate the substantial initial oil input to Astarte followed by two-fold decreases in naphthalene compound levels and significantly lesser deputation of the other aromatic series.   Residual aromatic levels in the second post-spill animals from Bay 10 are twice as high as the comparable Bay 9 animals.   These results parallel the absolute oil level results (Figure 3.116), which indicate that between the first and second post-spill samplings little deputation of oil from Bay 10 animals was observed.

3.4. 4.3 Bay 7

3.4.4.3a Oil Concentrations by UV/F

Astarte oil equivalents concentrations were 2.2 (.38,
6.4) µg/g pre-spill, 51 (12, 210) µg/g during the first
sampling, and 56 (31, 140) µg/g during the second sampling
(see Figures 3-111 and 3-117).

3.4.4.3b Oil Composition by GC[2]

Moderate concentrations of oil (approximately 100 ppm)
were acquired by Bay 7 Astarte, concentrations that remained
stable over the first two weeks after the spill. At the time
of initial sampling (September 1-3), oil residues in Bay 7
animals were well degraded (ALK/ISO = 0.2) and well depleted
in light aromatics. Thus, a greatly accelerated in vivo
microbial degradation is confirmed for Astarte versus the
other bivalves in that initial oil residues from Bay 7 Mya,
Serripes, etc. initially contained substantial n-alkane
character in the $C_{14}-C_{20}$ region. That the extent of micro-
bial modification of oil in Bay 7 is much greater than the
Bay 10 **animals** also sampled on September 1 may be related to
the overall levels of acquired petroleum (vs. higher levels
in Bay 9 and 10). Nevertheless, Astarte bivalves are capable
of more rapid in vivo microbial degradation than the other
species studied.

3.4.4.4c Aromatic Hydrocarbon Composition by GC[2]/MS

The Bay 7 GC[2]/MS results (Figure 3.118) agree quite
well with the Mya (Figure 3.83) and Serripes (Figure 3.97)
results in that the two-week oil residuals are characterized

TISSUE
PLOTS
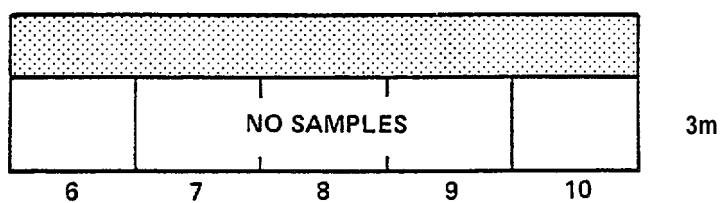
PRESPILL
17 AUG 81
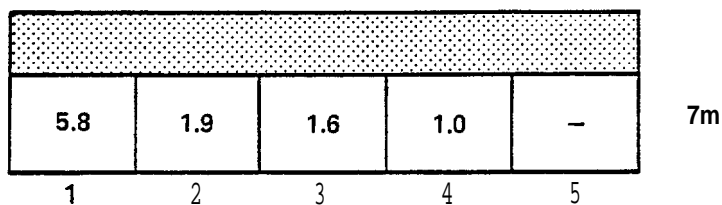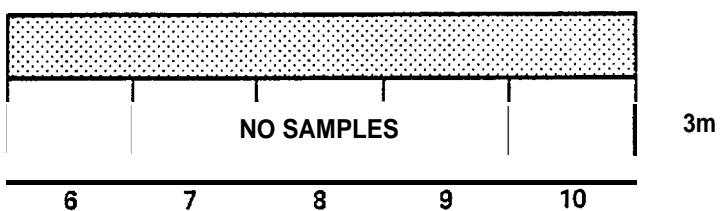
NO SAMPLES   3m

| 6 | 7 | 8 | 9 | 10 |

| 5.8 | 1.9 | 1.6 | 1.0 | — | 7m   2.2 (.38, 6.4)
| 1 | 2 | 3 | 4 | 5 |

FIRST POSTSPILL
1 SEP 81

NO SAMPLES   3m

| 6 | 7 | 8 | 9 | 10 |

| 90. | 6.1 | 105. | 58. | 96. | 7m   51. (12, 210)
| 1 | 2 | 3 | 4 | 5 |

SECOND POSTSPILL
11 SEP81

NO SAMPLES   3m

| 6 | 7 | 8 | 9 | 10 |

| — | 118. | 28. | 53. | 57. | 7m   56. (31, 140)
| 1 | 2 | 3 | 4 | 5 |
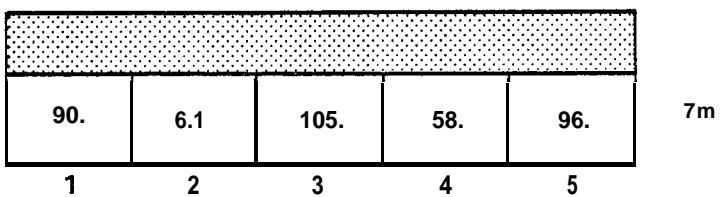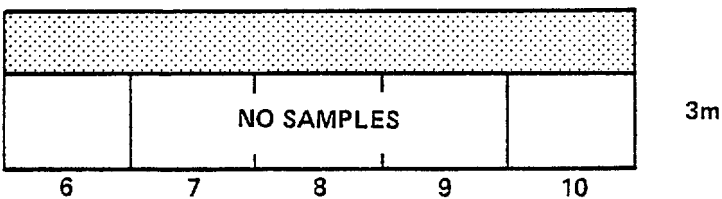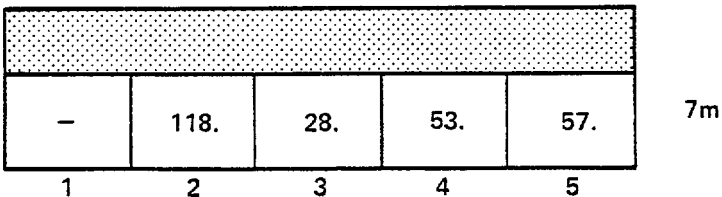
*95% Confidence Limits

Figure 3.117, Concentrations of Oil in Astarte borealis, Bay 7 by UV/F (μg/g).
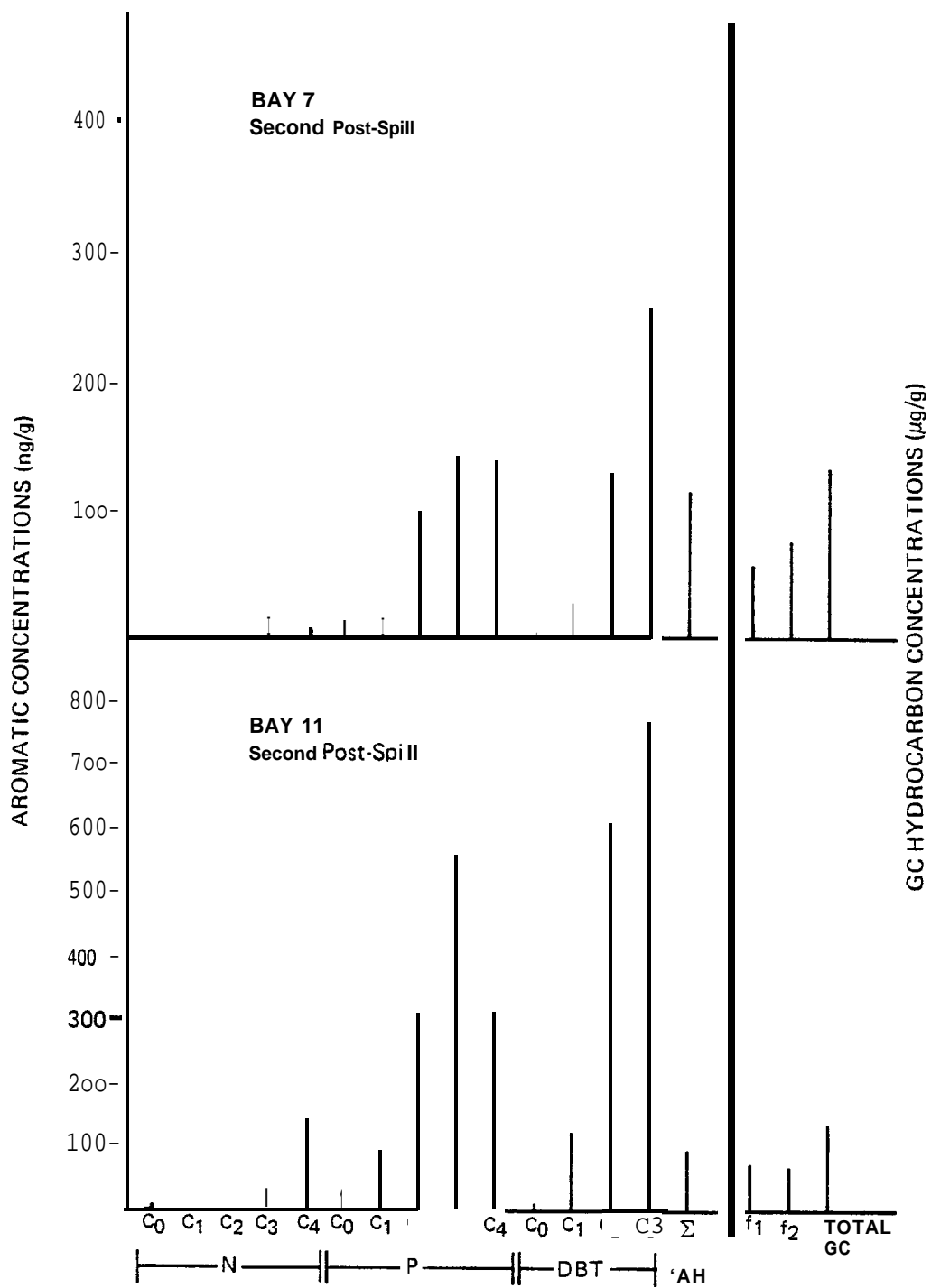
Figure 3.118. *Astarte* Aromatic Profiles (Bays 7 and 11).

largely by phenanthrene series (0.4 ppm) and dibenzothiophene series (0.5 ppm) compounds. No naphthalene compounds are observed in the two-week samples probably owing to low initial uptake of these water-soluble aromatics, as was the case with Mya and Serripes from Bay 7.

3.4.4.4 Bay 11

3.4.4.4a Oil Concentrations by UV/F

Bay 11 clams again contained 0.47 (.13, .92) μg/g of oil equivalents before the surface oil spill, a level of 2.7 (2.2, 3.4) μg/g during the first post-spill, and then an increase to 140 (50, 390) μg/g oil by the second post-spill sampling. This is the familiar pattern seen in all clams for Bay 11 (see Figures 3-111 and 3-119).

3.4.4.4b Oil Composition by GC^2

The one-day post-spill (i.e., surface oil spill - 8/19) animals from Bay 11 were devoid of any detectable petroleum. The second post-spill animals exhibit a GC^2 pattern very similar to that for Serripes (Figure 3.99) illustrating the predominance of isoprenoids in the $n-C_{13}$ to $n-C_{19}$ range, the persistence of n-alkanes in the $n-C_{21}$ to $n-C_{34}$ region, and the substantial UCM distribution. Indeed, the second post-spill animals are 88 percent comprised of UCM material. Aromatic GC^2 traces illustrate the alkylated phenanthrene/ dibenzothiophene predominance in the GC^2 traces.

TISSUE PLOTS
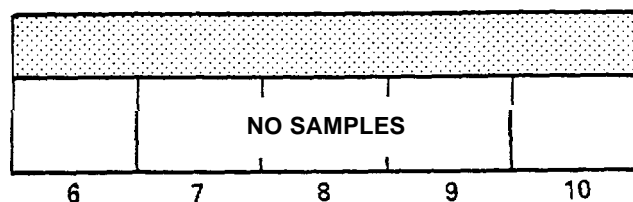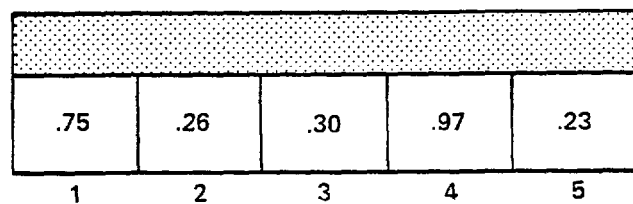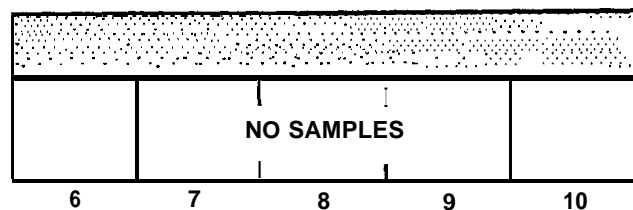
3m

7m   .47 (.13, .92)*

.75	.26	.30	.97	.23
1	2	3	4	5

**FIRST POSTSPILL
25 AUG 81**

3m

7m   2.7 (2.2, 3.4)

2.8	2.2	2.8	3.5	2.4
1	2	3	4	5

**SECOND POSTSPILL
11 SEP 81**

3m

7m   140. (50, 390)

70.	161.	316.	107.	—
1	2	3	4	5
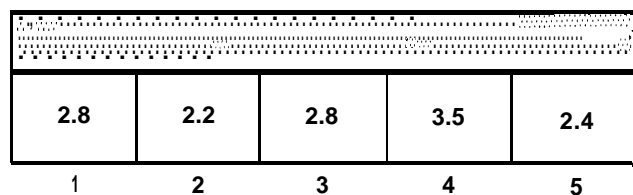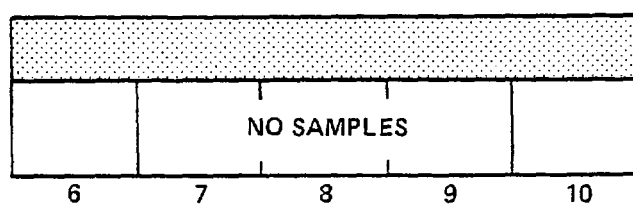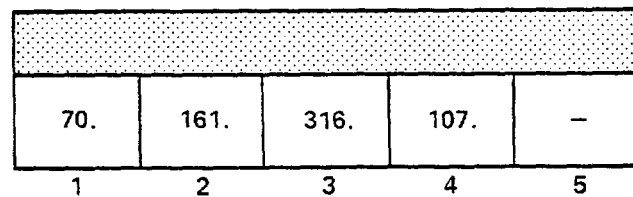
*95% Confidence Limits

Figure 3. I 19. Concentrations of oil in Astarte borealis, Bay 11 by UV/F (µg/g).

3.4.4.4C Aromatic Hydrocarbon Composition by GC^2/MS

The second post-spill sampling from Bay 11 illustrated the similar trends as for **Mya, Serripes,** and **Macoma;** i.e. , a naphthalene-depleted aromatic hydrocarbon assemblage characterized by **alkylated** phenanthrene (1.2 ppm) and **alkylated** dibenzothiophene (1.5 ppm) compounds (Figure 3.118). Levels of aromatics in Bay 11 animals are considerably higher than the Bay 11 **Macoma** and **Mya** sampled at the same time, but similar to **Serripes** levels (see Figure 3.97 bottom).

3.4.4.5 UV/F vs. GC^2 Analysis

Linear regression analysis of **Astarte** UV/F data versus GC^2 data is quite reasonable, Figure 3.120, with minimal background contribution by GC^2 or **UV/F.** Individual tissue plot stations show that **UV/F** measurements were low for the respective values determined by GC^2 in two of three stations. The station off the graph also contained an inexplicably high f2 fraction concentration.

3.4.5 Nuculana minuta

UV/F and GC^2 analyses were performed on 12 samples of this species. **GC^2/MS** analyses were conducted on 2 samples.

3.4.5a Oil Concentrations by UV/F (All Bays)

Nuculana sp. clams were analyzed by stratum poolings rather than by each of five tissue plot stations within a stratum, due to the scarcity of these clams found in the
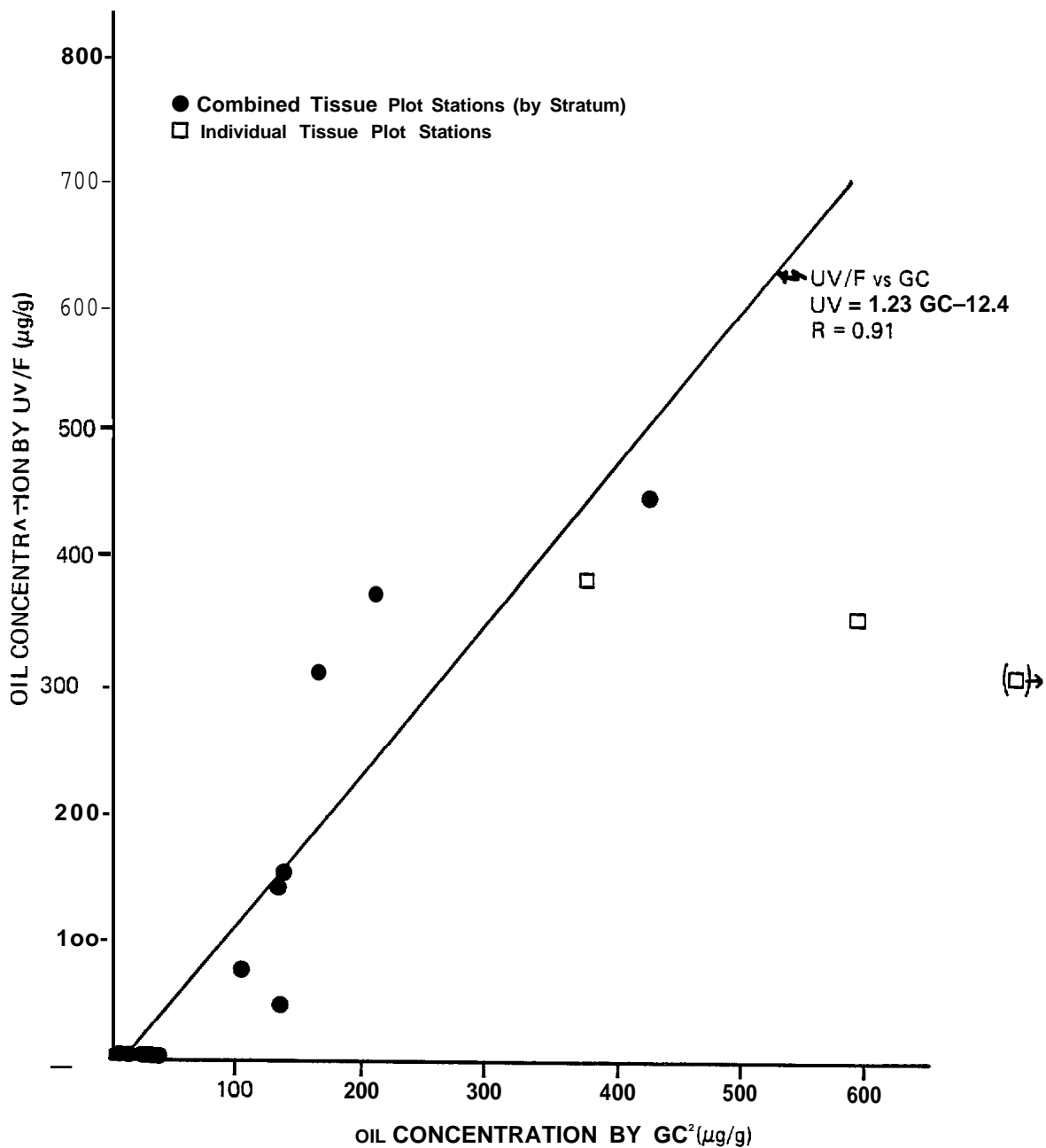
Figure 3,120. Regression of *Astarte* UV/F vs GC2 Data.

four bays. Pre-spill concentrations were similar in each
bay, ranging from 1.1 to 1.5 µg/g. Uptake patterns for each
bay parallel those demonstrated by Macoma rather than for
the filter feeding Mya and Serripes. Bay 9 first post-spill
clams contained 33.0 µg/g of oil and increased to 616 µg/g
of oil during the second post-spill sampling. Bay 10 first
post-spill animals contained the highest Nuculana levels,
442 µg/g of oil and decreased slightly to 337 µg/g by the
second post-spill. Bay 7 clams initially accumulated 41.2 µg/g
of oil during the first post-spill period (O-3 days) and
increased to 87.3 µg/g during the subsequent two weeks (i.e. ,
second post-spill). Bay 11 contained 11.3 µg/g of oil at
the time of the first sampling and increased to 429 µg/g of
oil by the second post-spill. This pattern, again, was
found with Macoma (see Figures 3-103 and 3-121 to 3-124).

3.4.5b Oil Compositions by GC^2 (All Bays)

GC^2 profiles resemble those for Macoma. The composi-
tion of the oil initially acquired by Nuculana either at the
30 ppm level in Bay 9 or the 440 ppm level in Bay 10 is a
slightly biodegraded oil (18/phy = 0.9 @ Bay 10; ⁻1.7 @
Bay 9; = 0.6 Bay 7) with a CPI (1.3) influenced by odd carbon
terrigenous n-alkanes. The second post-spill samplings
indicate further biodegradation (18/phy = 0.25; Bay 9) of
accumulated oil residues. The oil residues found in Bay 11
Nuculana in the second post-spill sampling is well biodegraded
(18/phy = 0.2). A typical saturated hydrocarbon sequence is
illustrated for Bay 10 in Figure 3-125.
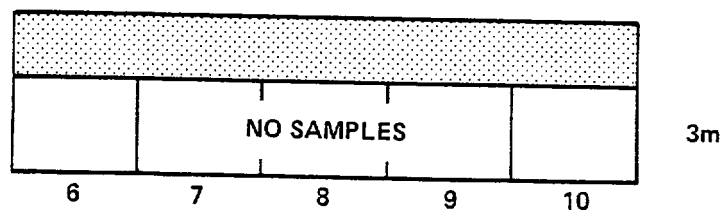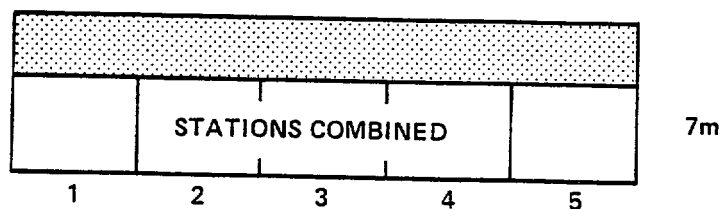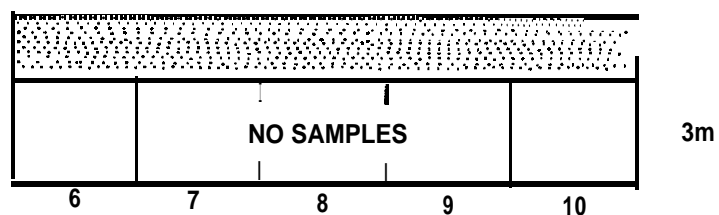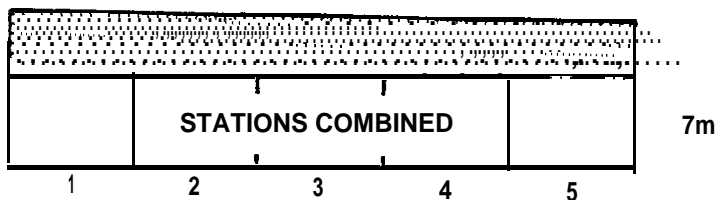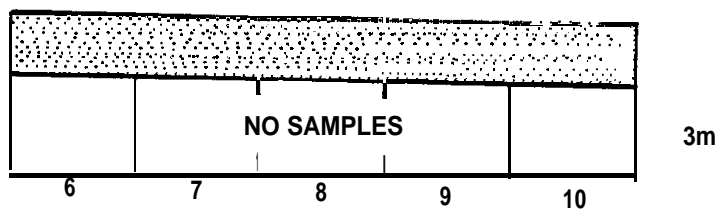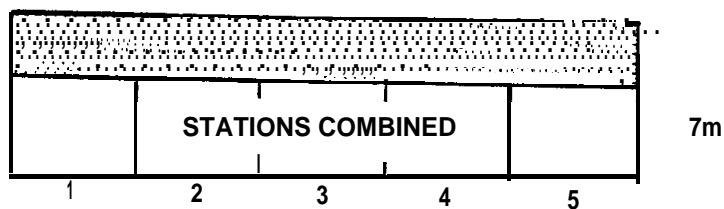
Figure 3.121, Concentrations of oil in <u>Nuculana</u>, Bay *9* by UV/F (μg/g).
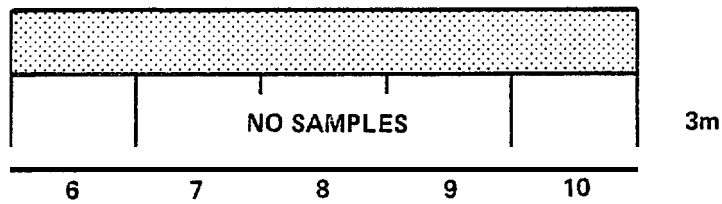
TISSUE
PLOTS

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m   1.4

1   2   3   4   5

FIRST POSTSPILL
1 SEP 81

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m   441.

1   2   3   4   5

SECOND POSTSPILL
12 SEP 81

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m   337.

1   2   3   4   5
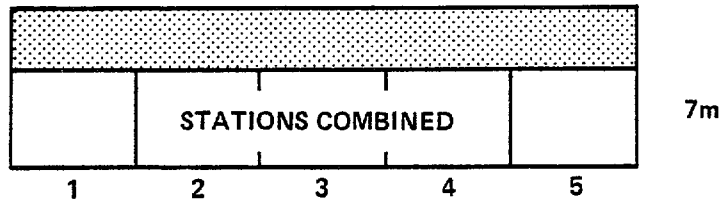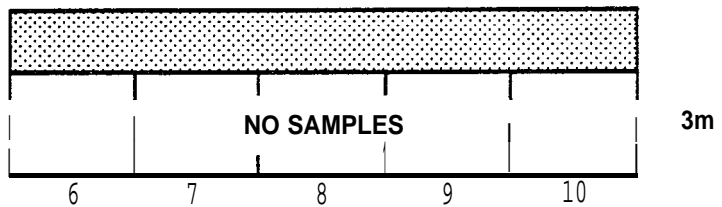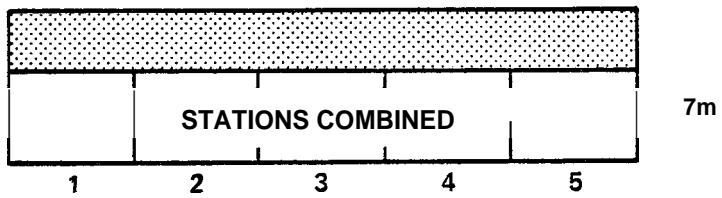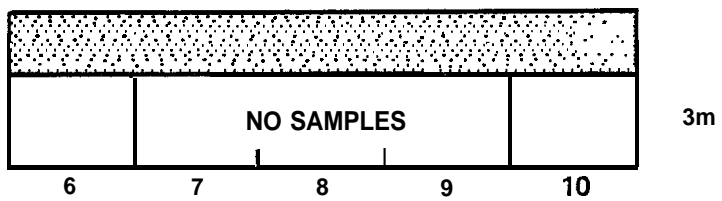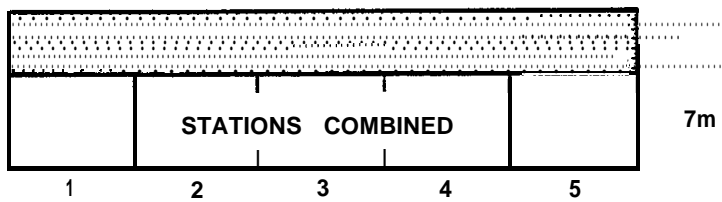
Figure 3.122. Concentrations of oil in Nuculana, Bay 10 by UV/F (μg/g).
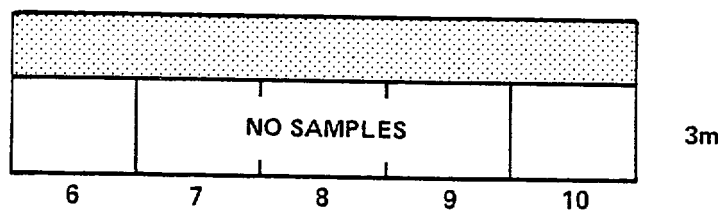
TISSUE
PLOTS

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m

1   2   3   4   5

1.2

FIRST POSTSPI LL
1 SEP 81

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m

1   2   3   4   5

41.

SECOND POSTSPI LL
11 SEP 81

NO SAMPLES   3m

6   7   8   9   10

STATIONS COMBINED   7m

1   2   3   4   5
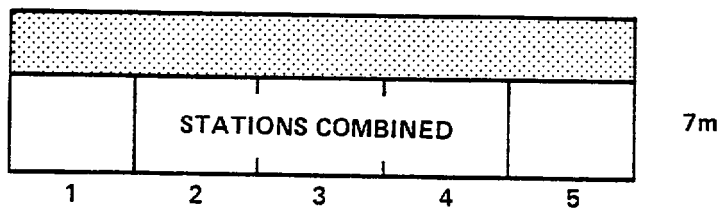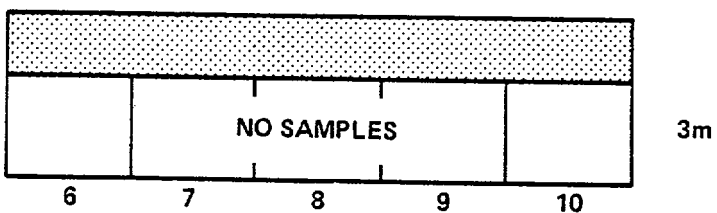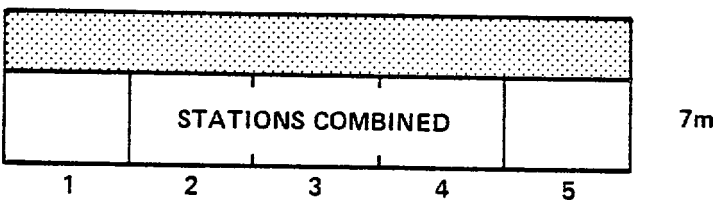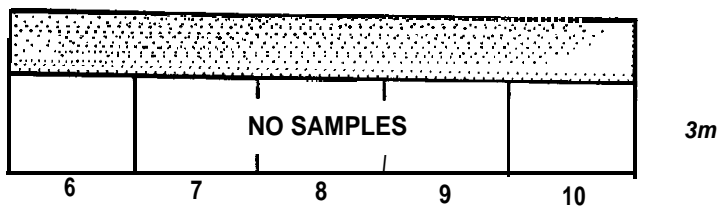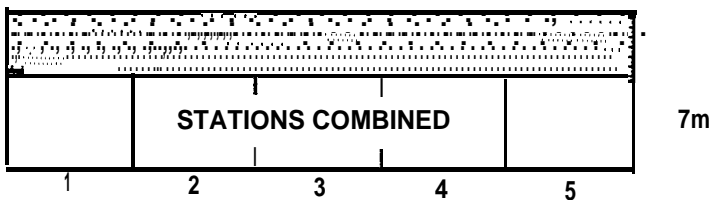
87.

Figure 3.123. Concentrations of oil in Nuculana, Bay 7 by UV/F (#g/g).
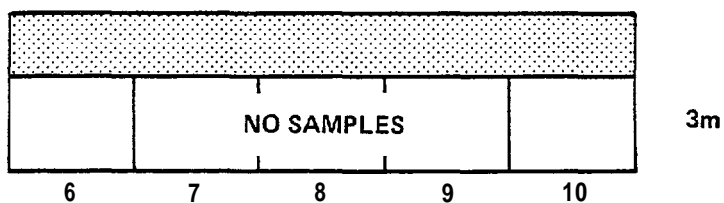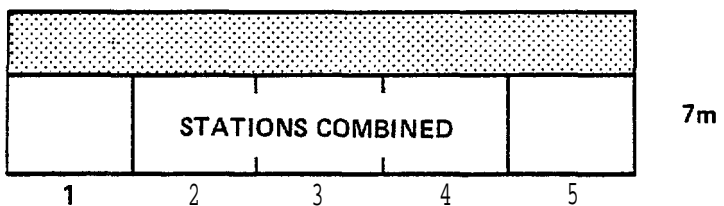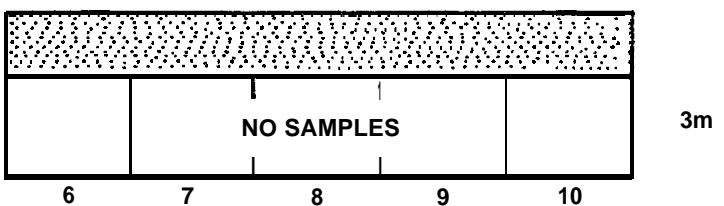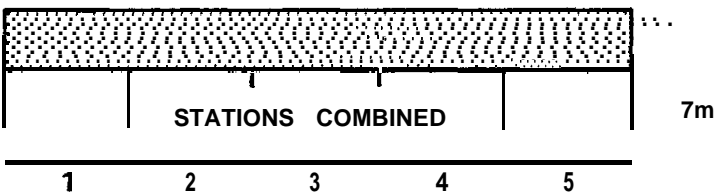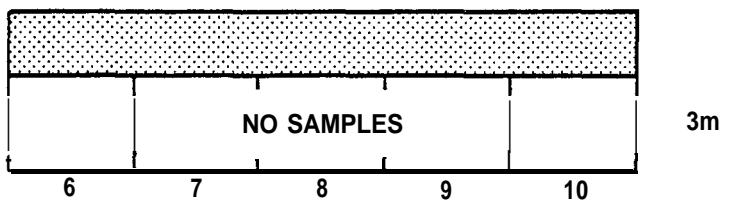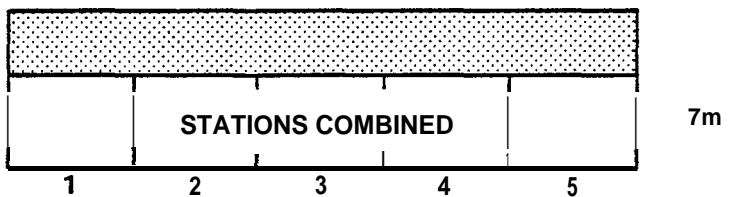
Figure 3.124. Concentrations of oil in <u>Nuculana</u>, **Bay 11 by** UV/F (μg/g).

Figure 3.125. Saturated hydrocarbon GC2 profiles of Nuculana minuta. (Bay 9).

3.4.5c Aromatic Hydrocarbon Composition by GC^2/MS

тwo **samples of** <u>Nuculana</u> (Bay 9 and Bay 11, second post spill) were analyzed by GC^2/MS (Figure 3.126). The Bay 9 sample contained sizable quantities of all aromatic hydro- carbon compounds (except **alkylated benzenes**), thus indicating either lack of preferential deputation of naphthalenes in contrast to results for the other species, *or* uptake of unweathered oil from contaminated sediments. In view of the fact that sediment aromatic profiles do not reveal abundant naphthalene compounds, the former explanation is favored.

Bay 11 <u>Nuculana</u> profiles, on the other hand, do not show any naphthalene compounds in tissues. This is con- sistent with the probable transport of oil to the Bay 11 benthos via beach erosion wherein naphthalenes are presumably solubilized and thus removed from the bulk sediment-bound oil. These Bay 11 results are consistent with second post-spill <u>Macoma</u>, <u>Serripes</u>, and <u>Mya</u> results. Absolute levels in Bay 11 aromatics in <u>Nuculana</u> are similar to those in <u>Mya</u> and <u>Macoma</u>, but are less than those in <u>Serripes</u> and <u>Astarte</u>.

3.4.5d <u>UV/F vs. GC^2 Analysis</u>

In this species, linear regression analysis (Fig. **3.127)** demonstrates the added sensitivity obtained by GC^2 for samples with minimal available tissue (slope = 0.84). The y-intercept of -40.4 again reflects most likely a biogenic background observable by GC^2. No individual tissue plot stations are available as this scarce clam was analyzed by stratum only.

Figure 3.126. *Nuculana* Aromatic Hydrocarbon Profiles.

AROMATIC CONCENTRATIONS (rig/g)

GC HYDROCARBON CONCENTRATIONS (µg/g)
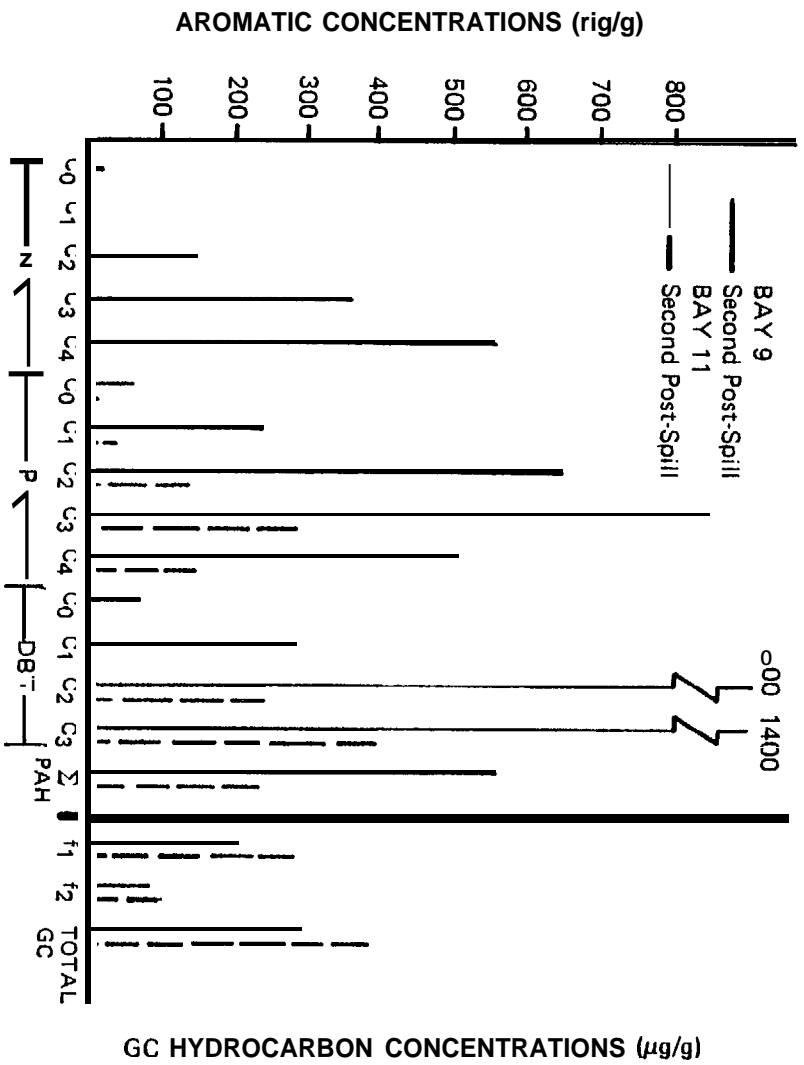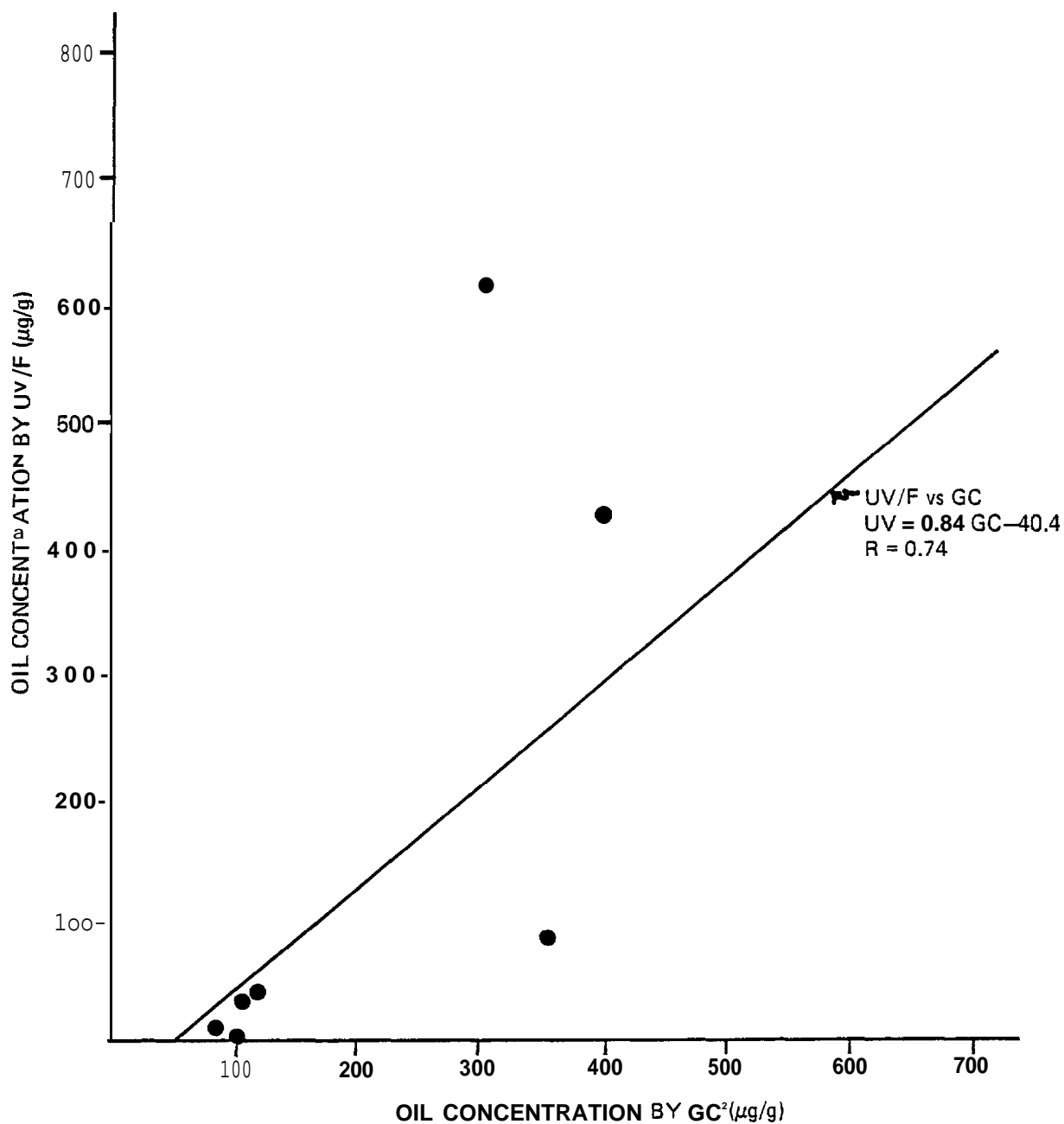
Figure 3.127. Regression of *Nuculana* UV/F vs GC2 Data.

3.4.6 Results by Bay (Table 3-24)

3.4.6.1 Bav 9

Prespill hydrocarbon concentrations in Bay 9 for all
five species of bivalves range from 0.35 µg/g to 1.3 µg/g.
First postspill accumulation of oil depends primarily upon
upon the assimilation pattern of the species of clam collected.

Along the offshore stratum (7m), Serripes and Astarte
both accumulated ∿500 µg/g of oil within 1 day of the
dispersed oil spill. Mya contained ∿120 µg/g of oil along
the 7m stratum, and ∿215 µg/g of oil along the 3m stratum.
Macoma and Nuculana follow the second assimilation pattern
(i.e., lower initial uptake) containing ∿75 µg/gm and
33 µg/g oil, respectively, by the first post-spill.

The second post-spill oil concentrations show a consist-
ent decrease in the Mya, Serripes, and Astarte **animals, to**
∿130µg/g **oil** for all species. On the other hand, concentra-
tions of oil increase in the Macoma and Nuculana clams which
contain the highest amounts of oil measured in Bay 9 animals:
836 µg/g and 615 µg/g, respectively. Note that the deposit
feeders continue to acquire oil while the filter feeders
decrease. This clearly demonstrates that a particular species'
feeding and pumping habits and its response to high concentra-
tions of oil in the water need to be considered if one is to
accurately describe the spill impact on the bay.

3.4.6.2 Bay 10

Bay 10 pre-spill hydrocarbon concentrations are also
low, ranging from 0.43 µg/g to 1.4 µg/g for all species.

TABLE 3-24

SUMMARY OF OIL CONCENTRATIONS[a] IN TISSUES BY BAY
(in µg/g dry weight)

SPECIES	STRATUM	BAY 9			BAY 10		
		PRE-SPILL	FIRST POST-SPILL	SECOND POST-SPILL	PRE-SPILL	FIRST POST-SPILL	SECOND POST-SPILL
Mya truncata	7m	0.35 (.22, .49)	121 (51, 290)	114 (90, 140)	0.57 (.42, .74)	277 (180, 420)	157 (110, 230)
	3m	0.40 (.25, .56)	215 (130, 350)	135 (120, 150)	0.78 (.55, 1.0)	368 (290, 460)	131 (96, 178)
Serripes groenlandicus	7m		186 (110, 330)	97 (59, 160)		329 (240, 460)	141 (110, 180)
	3m airlift			160 (120, 210)	–	698 (500, 970)	177
	7m	0.68 (-.02, 1.9)	482 (340, 680)	116 (69, 190)	1.4 (.40, 3.0)	278 (220, 350)	149 (130, 170)
Macoma calcarea	7m	0.73 (.33, 1.2)	75 (36, 150)	836 (610, 1140)	2.1 (1.0, 3.6)	406 (241, 680)	440 (250, 760)
	3m						
Astarte borealis	7m	0.81 (.44, 1.3)	463 (270, 800)	171 (88, 330)	0.43 (.25, .64)	364 (320, 410)	310 (210, 460)
	3m						
Nuculana minuta	7m	1.3	33.0	615.6	1.4	441.5	336.7
	3m						

[a] Geometric mean (lower 95% confidence limit, upper 95% confidence limit).

TABLE **3-24** (CONT.)

SPECIES	STRATUM	BAY 7			BAY 11		
		PRE-SPILL	FIRST POST-SPILL	**SECOND** POST-SPILL	**PRE-SPILL**	FIRST POST-SPILL	SECOND POST-SPILL
Mya truncata	**7m**	0.34 (.21, 4.8)	114 (64, 210)	47 (31, 70)	0.43 (.33, .53)	2.0 (1.2, 3.1)	93 (73, 120)
	31a						
Serripes groenlandicus	**7m**						
	3m airlift						
	7m	1.2 (1.2, 1.3)	517 (360, 750)	73 (31, 170)	1.6	6.0 (.19, 41)	394 (200, 780)
Macoma calcarea	**7m**	1.0 (.88, 1.2)	82 (60, 112)	85 (39, 190)	2.5 (.05, 10)	24 (14, 42)	246 (76, 790)
	3m						
Astarte borealis	**7m**	2.2 (.38, 6.4)	51 (12, 210)	56 (31, 140)	0.47 (.31, .92)	2.7 (2.2, 3.4)	140 (50, 390)
	3m						
Nuculana minuta	**7m**	1.2	41.2	87.3	1.1	11.3	428.9
	3m						

[a]Geometric mean (lower 95% confidence limit, upper 95% confidence limit).

The bivalves generally contain more oil in the 3m stratum
(inshore), but only for **Serripes** is the increase signifi-
cantly different between strata. Except for **Nuculana,** all
species **follow** the accumulation patterns described for Bay 9.
Within the 7m stratum Mya and Serripes contain, on the
average, 280 µg/g and 300 µg/g of oil respectively by the
first post-spill sampling, and these concentrations drop
as deputation proceeds to 160 µg/g and 145 µg/g of **oil** after
2 weeks. **Within** the 3m stratum, these two species contain
370 µg/g and 700 µg/g of oil respectively, which drops to
130 µg/g and 150 µg/g of oil by the second **postspill, reflect-**
ing the transient nature of a **wide** range (400-700 ppm) of **ini-**
tially acquired **oil.** Astarte initially acquired a comparable
360 µg/g concentration of **oil,** which then was maintained at
310 µg/g through the second **postspill.** **Macoma** contains more
oil when first sampled in this bay than in Bay 9. However,
Bay 10 was sampled three days later for **Macoma** than Bay 9,
thereby giving the deposit feeders more time for oil acquisi-
tion. **Nuculana** appeared to behave differently in Bay 10 as
compared to all other bays, having acquired a large amount of
oil (440 µg/g) initially, which then decreases to 340 µg/g
of oil in the second post-spill sampling. However, the samples
were obtained three days **later** in Bay **10** than in Bay 9.

   Mya clams were exposed to and/or acquired more oil in
Bay 10 than Bay 9. Serripes also acquired more oil in
Bay 10. This increased Bay 10 accumulation was observed
despite the fact that Mya and Serripes were sampled 1-2 days
later in Bay 10 than in Bay 9. (These bivalves depurate with
time rather than increase **their** body burdens as do the deposit
feeders). As was observed in Bay 9, the deposit feeders
Macoma and **Nuculana** do not illustrate marked deputation
between the first and second post-spill sampling. However,
Astarte shows no inclination to depurate accumulated oil as
was observed in Bay 9.

3.4.6.3 Bay 7

Bay 7 was designated the "control" bay. Pre-spill
concentrations are equivalent to the other three bays.
First post-spill values (August 31 or September 1), though,
show that oil did enter into the bay, and values for all
species other than Serripes are lower in Bay 7 than in 9 or
10. The large initial Serripes accumulation is an enigma
which requires laboratory verification studies. Note that
as the sediments of Bay 7 are "clean," Macoma, Astarte, and
Nuculana values are roughly invariant with time, indicating
that levels of oil in these animals are a product of initial
accumulation from the water column only and that even the
deposit feeders are influenced to a degree by water-borne oil.

3.4.6.4 Bay 11

Bay 11 results reflect the differences in oil behavior
between the dispersed oil spill Aug. 27, 1981 (Bays 9 and 10)
and the surface oil spill, Aug. 19, 1981 (Bay 11). Pre-spill
concentrations for all clams are at background levels, as are
most of the first post-spill oil concentrations (collected
August 25) suggesting that oil had not yet been transported
into the benthic environment. Macoma and Nuculana, the
deposit feeders, do appear to be acquiring oil during the
August 19-25 period, thus reflecting that transport of oil to
the benthos of Bay 11 begins in this time frame. Sediments
sampled on August 21 did not contain detectable levels of
oil. The second post-spill sampling (September 11) clearly
indicates that oil is present in all species of clams, ranging
from 93 µg/gm (Mya) to 400 µg/gm (Nuculana and Serripes).

3.4.7 Statistical Methodology for the Comparison of Benthic Animal Data

Concentrations of petroleum were measured in five species of benthic animals collected from five fixed sites (tissue plots) located along two depth strata in four experimental bays. Animals were collected during prespill, first postspill, and second postspill time periods. (Details of sampling were described in Section 2.1.) Depending on the abundance of a particular species and the nature of the sampling, 12 to 18 sample groups each containing one to five observations result.

As described for the sediments in Section 3.2.7, the concentrations of petroleum measured by UV/F expressed in µg/g dry weight were used for the analysis. Since the variances were found to be heterogeneous within a species, the data were transformed using the log transformation, $Z = LN (Xi + 1)$. The transformation reduced but did not remove all of the heterogeneity. The log transformed data sets were used in all statistical calculations. The means and 95% confidence intervals for each data group were calculated and the sample groups were tested for statistically different means using the methods described for the sediments. Summaries of the statistical data and comparisons of the benthic animal data appear in Appendix A.

3.4.8 Tissue Intercalibration Results (ERCO Results)

Four samples were prepared for purposes of intercalibrating analytical activities betwen ERCO and CWS. These included one post-spill tissue homogenate (urchin), a Mya extract spiked with oil, an oiled urchin extract, and an

oil-spiked hexane sample. The homogenate and two spiked extracts were analyzed by UV/F and GC^2 in duplicate and three GC^2/MS analyses were performed. The ERCO results are presented in Table 3-25. A comparison of intercalibration data is available from R. Englehardt (DIAND, Ottawa).

TABLE 3-25

INTERCALIBRATION RESULTS

	1 (urchin homogenate)	2 (spiked mya extract)		3 (spiked urchin extract)		4 (oil spiked hexane)
	A	A	B	A	B	A
Cone (UV)[a] (actual concentra-tion)[b]	218.0	21.2 29.2	20.8	9.4 20.7	11.7	27.5 34.1
Alkanes[c]						
C_{14}	.81	.07	.08	.03	.03	.16
C_{15}	1.5	.15	.17	.12	.11	.18
C_{16}	1.7	.13	.13	.06	.06	.19
C_{17}	2.1	.19	.20	.08	.06	.19
PRIS	7.2	.37	.37	1.7	1.6	.08
C_{18}	1.5	.13	.14	.07	.07	.17
PH Y	.93	.08	.08	.04	.04	.11
C_{19}	1.9	.15	.15	.07	.07	.14
C_{20}	1.6	.12	.13	.06	.06	.16
C_{25}	.95	.18	.20	.07	.08	.09
C_{27}	.75	.21	.24	.06	.08	.07
Aromatics[d]						
Naphthalene	nd	--	2.5	--	nd	
C_1N	nd	--	1.8	--	nd	
C_2N	130	--	12.3	--	7.6	
C_3N	210	--	18.5	--	9.5	
C_4N	160	--	9.3	--	3.8	
Fluorene	nd	--	nd	--	nd	
C_1F	nd	--	nd	--	nd	
C_2F	30	--	3.1	--	nd	
C_3F	90	--	3.1	--	nd	
Dibenzo-thiophene	60	--	1.6	--	nd	
C_1DBT	120	--	12.3	--	3.8	
C_2DBT	260	--	21.5	--	5.7	
C_3DBT	220	--	24.6	--	5.7	
Phenan-threne	90	--	4.6	--	1.9	
C_1P	140	--	12.3	--	3.8	
C_2P	240	--	13.8	--	3.8	
Fluoran-thene	330	--	4.6	--	nd	
Pyrene	410	--	6.2	--	nd	

[a,c] Sample 1 µg/g
Sample 2,3,4 µg/ml

[b] Englehardt, personal communication.

[d] Sample 1 rig/g
Sample 2,3,4 ng/ml

nd = less than 1 rig/ml

SECTION FOUR

The results of the analytical data previously presented considerably increase our knowledge of the differential fate and behavior of chemically dispersed and surface oil. Furthermore, the transport of oil to the benthos, its route of transport to benthic organisms (oil acquisition) and the species-specific chemical nature of biotal oil deputation are revealed in the wealth of data obtained in this study. We will discuss some of the most important observations and trends here as they pertain to the behavior of oil in the experiments, and to specific important transport paths and biotal impacts.

The quantities of oil driven into the water **column as a result of chemical** dispersion are far greater than those that result from transport of untreated surface oil into the water column. Concentrations of chemically dispersed oil ranged from 1 to greater than 50 ppm (~100 ppm) during the dispersed oil discharge and for as long as twelve hours after discharge ceased at some points in Bay 9. Differential movement of oil released at different points along the diffuser resulted in direct northward movement of oil at greater depths of release (10 m,) and initial southerly movement of oil at shallower depths followed by subsequent reversal of direction and "reinvasion" of Bays 9 and *10* four hours after formal oil/dispersant discharge ceased. The dispersed oil plume formed a very stable layer of oil in the water column for perhaps 6-13 hours after dispersal. Dispersed oil droplets carried by strong shore currents were advected for considerable distances without a significant change in the

composition of the oil. Whether this occurred due to the stability of the small ($\sim$10 urn) oil droplets, thus retarding fractionation (i.e., dissolution or evaporation), or whether particulate and dissolved parcels of oil traveled coherently due to strong advection (0.5 knot currents), is difficult to ascertain. Results of large volume water samplings which were taken outside of these concentrated plumes and after the passage of the highest concentrations indicated that a physical-chemical fractionation of hydrocarbon compounds did occur. It is, however, quite significant that fresh oil with its full suite of low molecular weight saturated and aromatic components persisted as a coherent plume for considerable periods of time (6-13 hours), apparently cut off from evaporative loss from either the dissolved state or by advection to the surface. Indeed, confirmation of this coherent oil layer was made by fluorescence profiling and by discrete sampling, sometimes indicatinga tenfold increase in water-borne oil concentrations within a water layer sandwiched by lower concentrations of more highly weathered oil. The persistence of low molecular weightsaturates(C_6-C_{10} alkanes) and alkylated benzenes and naphthalenes in the plume in similar proportion to the total petroleum in the neat oil was unexpected. Surely the subsurface release of dispersed oil accounted for this. A surface release followed by application of chemical dispersants would have allowed some loss of light aromatics to occur by evaporation.

The very striking similarity between the BIOS dispersed oil plume behavior and that observed in the Ixtoc I spill (Boehm and Fiest, 1982; Walter and Proni, 1980) is of no small importance. A subsurface release of oil that creates small oil droplets either through shear (Ixtoc) or through stabilization through chemical dispersion (BIOS) with resulting droplets advected by strong currents, results in subsurface

coherent plumes of unweathered fresh oil with a full contingent of toxic aromatics. The similarities between the two events is also striking given the 25° C water column temperature differential between Gulf of Mexico and Arctic waters. Of course these initial high levels of oil (roughly 10 ppm in the Ixtoc I and 10 ppm and greater in the BIOS scenarios) will eventually be reduced through dilution and diffusion even if the coherent subsurface plume persists as it did for 20 km or so in the Ixtoc I spill.

During and after the dispersed oil experiment there was little evidence for either the large scale beaching of dispersed oil or the surfacing, in the water column, of dispersed oil. However, both phenomena did occur to minor extents and resulted in some important information. Oil that was found adhering to the Bay **9** beach was present at low levels **(5-10** ppm**)**. The oil had weathered significantly, due mainly to losses of low molecular weight components. Both the concentration of oil on the beach and its composition were nearly identical to those found in the offshore benthic sediments implying a detectable but low sorptive affinity of dispersed oil. Oil which did appear to have coalesced at the sea surface was highly weathered through loss of low boiling saturates and aromatics. The state of weathering of this surface oil sampled several hours after initial dispersed oil discharge, was equivalent to that of nine day old beached surface oil (Bay 11). Thus it appears that the coalesced oil formed after solubles were stripped from the oil in the water column with the coalesced oil forming from a weathered residue.

Oil did impact the sediments of Bays 9 and 10 immediately after the dispersed oil spill where initially a significant amount of the sedimented oil (∿20%) resided in the surface

floe. Sedimentation rates were estimated to be in the 2-10 mg/m^2/day range. Subsequently, the floe was transported elsewhere, probably offshore, because floe from all bays sampled in the second post-spill period (September 11) was free of any detectable oil. Levels of oil in the sediments, however, remained elevated (1-5 ppm) in Bays 9 and 10 and although this dosing is considerably less than a "massive" dosing, it will continue to affect benthic biota for an unknown period of time. The overall sediment impact due to passage of dispersed oil through Bays 9 and 10 was minimal, with less than 1% of the discharged oil probably residing in the sediment at any time.

Results from the initial sampling of sediments indicated that 80% of the oil detected in the top O-3 cm was not associated with the floe. This is in contrast to results from other spills (e.g., Boehm et al., 1982) and to experimental tank studies (Gearing et al., 1980) in which most of the initially sediment-associated oil was in the floe layer. What appears to be occurring in the BIOS dispersed oil spill is a low level, direct and rapid penetration of dispersed oil into the bulk surface sediment, presumably a process mediated by the decrease of the oil's interracial tension due to chemical dispersion allowing for penetration of the solid interface and perhaps into interstitial waters. Indeed chemical results from polychaete analyses in Bays 9 and 10 (Norstrom and Engelhardt, 1982) revealed an initial uptake of an alkylated benzene and naphthalene (i.e. , water soluble fraction) enriched petroleum hydrocarbon assemblage in Bays 9 and 10 only, perhaps associated with interstial water penetration of fractions of the oil.

The Bay 7 "control" did receive 50-100 ppb of dispersed oil in the first few days after the discharge. This

quantity of oil was measured directly (Green et al., *1982)*
and was monitored indirectly through hydrocarbon body burdens
in filter-feeding bivalves (i.e. , Mya, Serripes). Direct
sediment analyses and indirect evidence from deposit feeding
animals (Macoma, Strongylocentrotus) indicate, however, that
oil impact to Bay 7 sediments was suite minimal with only
patchy low level inputs noted. The Bay 7 analytical results
point to an important conclusion regarding application
of UV/F and GC^2 techniques to the BIOS study. While
background (by UV/F) levels of "oil equivalents" in the
sediments was ∿0.5 ppm, many samples did exhibit post-spill
oil levels of 1.0-1.5 ppm. In this concentration range
levels were too low to unambiguously yield an oil/no oil
decision based on GC^2. Oil levels of ∿1.0 ppm would
contain individual component concentrations (i.e., n-alkanes)
of ∿.01 ppm (or *10* ng/g). Due to significant biogenic
background in the GC^2 traces, this level of individual
components was often too low to see in the GC^2 traces. Thus
UV/F becomes a key to assessing oil concentrations in sedi-
ments. However, in several cases in Bay 7 sediments, low UV/F
levels (∿0.3 ppm), generally associated with background
levels, were shown by GC^2 to contain small amounts of oil.
The weathering of oil while in transit **to Bay 7 with resulting
loss of water** soluble aromatics and a concomitant decrease in
UV/F response, caused whatever oil was seen in Bay 7 sediments
to be relatively enriched in saturates (not detectable by
UV/F). Thus the two techniques of UV/F and GC^2 proved to be
an extremely powerful complementary set.

Water-borne oil in Bay 11 was initially confined to the
surface (0-2 meters) layer during which time large scale
transport of oil to the benthos via sorption and sinking did
not occur. Through large volume water samples, low levels
(ppb) of oil were detected in mid depth and bottom waters

largely in a particulate form, prior to any possible cross
contamination from the dispersed oil spill occurring a week
later. That oil did impact the sediment in Bay 11 prior to
the dispersed oil spill is evident from uptake patterns of
all of the benthic animals, especially those of the deposit
feeders Macoma and Nuculana and of the filter-feeder Serripes
which all revealed uptake of oil, albeit at lower levels
relative to those which were acquired in the dispersed oil
scenario, prior to any possible cross contamination from
Bays 9 and 10. We do know that the dispersed oil's influence
was far ranging including a transient water column impact at
Bay 7 causing elevated levels of oil in all benthic biota,
especially the filter feeders Mya and Serripes. Thus it may
be logical to "subtract" the observed Bay 7 animal levels
from the Bay 11 values to derive a "pure" Bay 11 result for
the second post-spill sampling. Using this logic it can be
concluded that although low levels of oil are acquired in
Bay 11 by the filter-feeders, the major Bay 11 impact is to
the deposit feeders who are more closely linked to the
sediments and which acquire weathered oil from off of the
beach face.

The most significant findings of the study concern the
relationship between water-borne levels of oil, sediment
concentrations and levels in benthic biota. Initial uptake
of oil by Mya and Serripes is from the water column wherein
oil is acquired through pumping of contaminated seawater
through the gills. Most of this oil initially resides in
the animal's gut as confirmed through Serripes dissections.
Chemically, even the initial oil residues in the gut and
muscle tissue are different. The more water soluble aromatics
(napththalene, alkylated benzenes) are transported to the
muscle tissues (including gills) more rapidly, with the
phenanthrenes and dibenzothophenes preferentially located in

the gut.   During the first two weeks after the spill however,
it is these higher molecular weight aromatics which persist,
the water soluble aromatics being depurated more readily.
Initial levels of oil in filter feeders from Bay 7 are
equal or greater than those from Bays *9* and 10 where water
column levels of oil were 20 to 200 times as great.   Sediments
are ruled out as an oil-biotal intermediary due to the near
absence of oil in Bay 7 sediments.   Thus one must postulate
that while Mya and Serripes from Bays 9 and 10 either cease
pumping due to water column levels or die after initial
accumulation of oil, animals in low-to-moderately contaminated
waters continue to pump and acquire oil as long as it is
present in the water. At water column concentrations
of 50 μg/l (50 ppb) a clam (1 g dry weight) pumping at a
rate of 1 liter per hour would pass 1.2 mg of oil through
its body in 24 hours, more than enough to acquire a 100-500
ppm concentration.   As levels of oil in Bays 9 and 10 were
much higher, 1-50 ppm initially and 100-200 ppb for at least
a day to a day and a half after cessation of the oil spillage,
opportunities for greater bioaccumulation in Bays 9 and 10
were available but were probably not achieved due to either
saturation in the gut, an inability to transport oil across
the membranes fast enough to acquire more oil, or a wholesale
cessation of pumping.

As Mya and Serripes acquire oil through the water
column, depurate 60-75% of it in two weeks time, Macoma and
Nuculana acquire oil mostly through the sediments.   Initially
low-to-moderate oil levels in animals increase in Bays 9 and
10 where sediment impacts are greatest, and in Bay 11 where
offshore movement of beached oil results in higher initial
(1 day) accumulation of oil than with the filter-feeders and
increasing levels with time.   GC^2 profiles show evidence
of uptake of oil from sediment rather than the water column

in those species after perhaps an initial (~30-50 ppm) water column uptake. Bay 9 and 10 deposit feeders continue to take up oil as evidenced by increasing absolute levels and maintenance of a relatively unbiodegraded GC2 profile and a low CPI (i.e., oil dominates terrigenous n-alkanes).

As previously discussed the two oil spill experiments conducted introduced oil into the nearshore system in two distinct manners. The Bay 11 surface oil (untreated) spill resulted in detectable water-borne oil concentrations only in the top meter or so of the water column (Green et al., 1982). That low levels of water soluble oil may have penetrated to the benthos during the first day or so following the spill can not be confirmed from direct chemical evidence of water samples, but may have occurred, causing the low initial increases in petroleum hydrocarbon levels and levels of water soluble aromatics in some of the filter feeders (Mya, Serripes, Astarte). That oil did impact the Bay 11 benthos as soon as one day after the spill is indicated by the uptake of oil by Macoma, Pectinaria and Strongylocentrotus revealed in the immediate post-spill period. Subsequent benthic impact of oil in Bay 11 is clearly indicated in increased sediment concentrations (~5 ppm) as well as by the increased uptake of oil by the deposit (detrital) feeders. The oil reaching the benthos during the 1 day to 3 week post-spill period was weathered due to evaporation/dissolution as evidenced by the loss of alkylated benzene and napthalene compounds relative to the spilled oil.

The uptake and deputation curves during the first several days are difficult to reconstruct due to differences in sampling times. For example, it is not clear whether higher levels of oil in Serripes in Bay 10 versus Bay 9 were

due to a combination of animal behavior and water column
concentration or due to the additional day during which they
acquired oil. Alternatively filter feeders may very well
have "shut down" their pumping systems in Bay **9**(or were
narcotized or killed outright) due to high water column
levels, while those animals in Bay 10 may have continued to
pump and acquire more oil. Indeed this seems to have been
the case in Bay 7. Low levels of oil (50-100 ppb) were
detected in Bay 7 two days after the spill (Green et al.
1982), as were these same levels in Bays 9, **10** and at
other Ragged Channel locations. Bay 7 <u>Serripes</u> were especially
efficient at concentrating oil from these lower water column
levels with oil residing primarily in the gut initially.
The fact that <u>Serripes</u> and <u>Mya</u> from Bay 7 were probably not
physiologically affected by those lower levels of oil
probably resulted in their normal pumping of water throughout
the first several days after the spill.

As alike as <u>Mya</u> and <u>Serripes</u> behave **vis-a-vis** routes of
oil uptake, they differ in the compositional nature of the
oil which they retain. During the two week post-spill
period of deputation, an <u>in vivo</u> biodegradation presumably
by a microbial population within the animals guts occurred
to a significant extent. At this point the similarity
between <u>Mya</u> a<u>nd Serrip</u>es erodes **because although on a gross
level both** species **depurated** oil, on   a   detailed   chemical
basis <u>Serripes</u> preferentially retained a high molecular
weight saturated hydrocarbon assemblage as well as the
higher **alkylated naphthalene,** phenathrene and **dibenzothio-**
phene compounds. <u>Mya</u> on the other hand depurated all
hydrocarbon components although the water soluble **alkyl**
benzenes and **naphthalenes** were depurated somewhat faster.

Thus as the exposure levels in the water column decreased, levels in <u>Mya</u> decreased as well as did the gross oil levels in <u>Serripes.</u> This plus the fact that whole, undegraded (microbial) oil resided in Bay 11, 9 and 10 sediments without a concomitant increase in concentrations in oil levels in the filter feeders effectively decouples sedimentary sources of hydrocarbons from these animals. This decoupling is accented by the fact that while oil residues in sediments were not degraded, residues in the animals were microbially degraded.

<u>Macoma</u>, <u>Nuculana</u>, <u>Strongylocentrotus</u> and <u>Pectinaria</u> clearly are influenced by sediment oil levels more so than those in the water column. Though there is some indication that low levels of soluble aromatics in the water were reflected in early oil compositions in the deposit feeders, steady uptake of sediment-bound oil by this group dominates. Thus the lack of detectable sediment-bound oil in Bay 7 is reflected in much lower petroleum body burdens in deposit feeders from this bay. Additionally over two weeks we see much less of an indication of microbial degradation in the Bay 9, 10 and 11 deposit-feeding animals due to the acquisition of undegraded oil from the sediments appearing as a constant compositional overprint. Furthermore, those aromatic hydro-carbon components longest lived in the sediments (i.e. , alkylated dibenzothiophene and phenanthrene compounds) steadily increase in the deposit feeders.

Thus the various filter feeders and deposit/detrital feeders reflect the fate of oil in the system quite well. The fact that the polychaete acquires whole oil, dominated somewhat by a water-soluble grouping of alkylated benzenes and napthalenes, may reflect the association of oil with interstitial waters in the upper sediment column.

Parallel behavior of filter-feeding versus detrital
feeding bivalves has recently been noted in an actual spill
(Boehm et al. 1982a). In this study the authors have found
that the benthic-dwelling Macoma balthica was slower to
initially acquire oil than was the filter-feeder Mytilus
edulis which resided in the phytal zone. After beaching and
erosional transport, and/or direct sedimentation of oil,
the petroleum body burden increased in Macoma and only
slowly decreased as the sediment levels dropped. Mytilus,
on the other hand, exposed to a massive initial amount of
water-borne oil, depurated rapidly and almost completely
over one year's time.

During the first two to three weeks after the spills
there was a notable lack of significant biodegradation of
oil in the water column and in the sediments. There is no
chemical evidence for the existence of biodegradation as a
removal mechanism with the short-term post-spill period
(3 weeks) either in the water column or in the sediment. One
would have predicted higher rates of biodegradation in surface
sediments, especially in the surface floe, but none was
observed through degradation of the "easily" degraded n-alkanes.
However, degradation of n-alkanes in the oil resulting in the
classic loss of n-alkane relative to isoprenoid and other
highly branched alkanes, is observed within Mya and Serripes
and to lesser extents in other benthic species. Rapid degrada-
tion of alkanes only occurs in vivo. Whether or not this
unique finding can be ascribed to microbiotal populations
within the organism itself, a likely mechanism, must be
independently confirmed. We suspect that given an unspecified
amount of time microbial populations will begin to utilize
the hydrocarbons as an energy source (i.e., biodegradation
will become more significant).

The use of a variety of biological monitors or sentinel
organisms in the BIOS study has served to both delineate oil
transport paths and changing environmental compartment
levels with time during the immediate post-spill (0-3 weeks)
period. Furthermore, this study has shown that although
similarly behaving animals (e.g. Mya/Serripes; Macoma/
Strongylocentrotus) may on a gross level appear to
act in concert, the details of in vivo modifications and
retentions of individual petroleum components are quite
different and may be intimately associated with long term
biological effects on the individual benthic species.

One question which persists is what transport processes
may act in the short term to move oil within the Ragged
Channel system. Evidence from the initial post-spill period
does indicate 1) that the oil contaminated floe is a transient
phenomenon, and 2) sediment concentrations tend to increase
with depth (i.e. , offshore). This implies that initial
deposition of oil increased with distance offshore and that
subsequent movement and transport of oil may cause more of a
benthic impact farther offshore into Ragged Channel. Of
course the movement of sediment-bound oil in Bay 11 is linked
to erosion of beached oil as well.

Thus it appears that the experimental spills in 1981
were an unqualified success in that 1) very important trends
in Arctic biotal uptake mechanisms and deputation trends
were revealed, 2) the lack of significance of sedimentation
of chemically dispersed oil was ascertained (<1%), 3) the
rapid penetration of small but significant quantities of
dispersed oil residues into benthic sediments (below the
floe layer) was established, 4) the coherent subsurface
movement of "fresh" dispersed oil without evaporation of
toxic components was observed, 5) the lack of significant

biodegradation in the 3 week post spill period was determined,
6) the <u>in vivo</u> biotal **microbial degradation of** oil **was**
observed, and 7) the relative retention of three-ringed
alkylated aromatic hydrocarbon and organic sulfur compounds
in tissues and in sediments was confirmed, thus implying
their use as long term markers of the oil in all environmental
compartments.

SECTION FIVE

SECTION FIVE

RESULTS (SHORELINE <u>STUDY</u>)

Samples from four pairs of 1980 oil test plots and
from ten 1981 plots/experiments were analyzed to determine
the detailed hydrocarbon composition of the residual oil,
dispersed oil, and chemically treated oils in the plots.
The extent of weathering of the oil was determined for each
sample. The 1981 samples were obtained at time intervals
including immediately following the initiation of the test
(**mixing,** dispersant application, etc.) and 8 and 40 days
later (see Figures 5-1 and 5-2 and Table 5-1). Surface and
subsurface samples were taken as part of the **resampling** of
the 1980 test plots (Figure 5-1 and Table 5-2). Additionally
six samples of beached oil from Bay 11 are included as are
six oil samples from the shoreline study.

5.1 Hydrocarbon   Concentrations

A **summary of the data on the gross compositional**
features (e.g., resolved by GC^2/FID) and total (i.e., by
microgravimetry) hydrocarbons are presented in Table 5-3
for all of the test plots and for samples of beached oil
from Ragged Channel Bay 11 (Nearshore Study, surface oil).
Residual concentrations in the 1980 backshore test plots
(T-1, T-2, **TE-1, TE-2**) remain high (10-25 mg/g) after a
year's exposure compared to ~10-30 mg/g when last sampled
in 1980. This indicates that the oil concentrations in the
backshore plots have not changed appreciably with time.
Additionally, there is only a minimal difference in oil
concentrations between surface and subsurface beach sediment
(no more than a factor of two decrease from surface to
subsurface) .
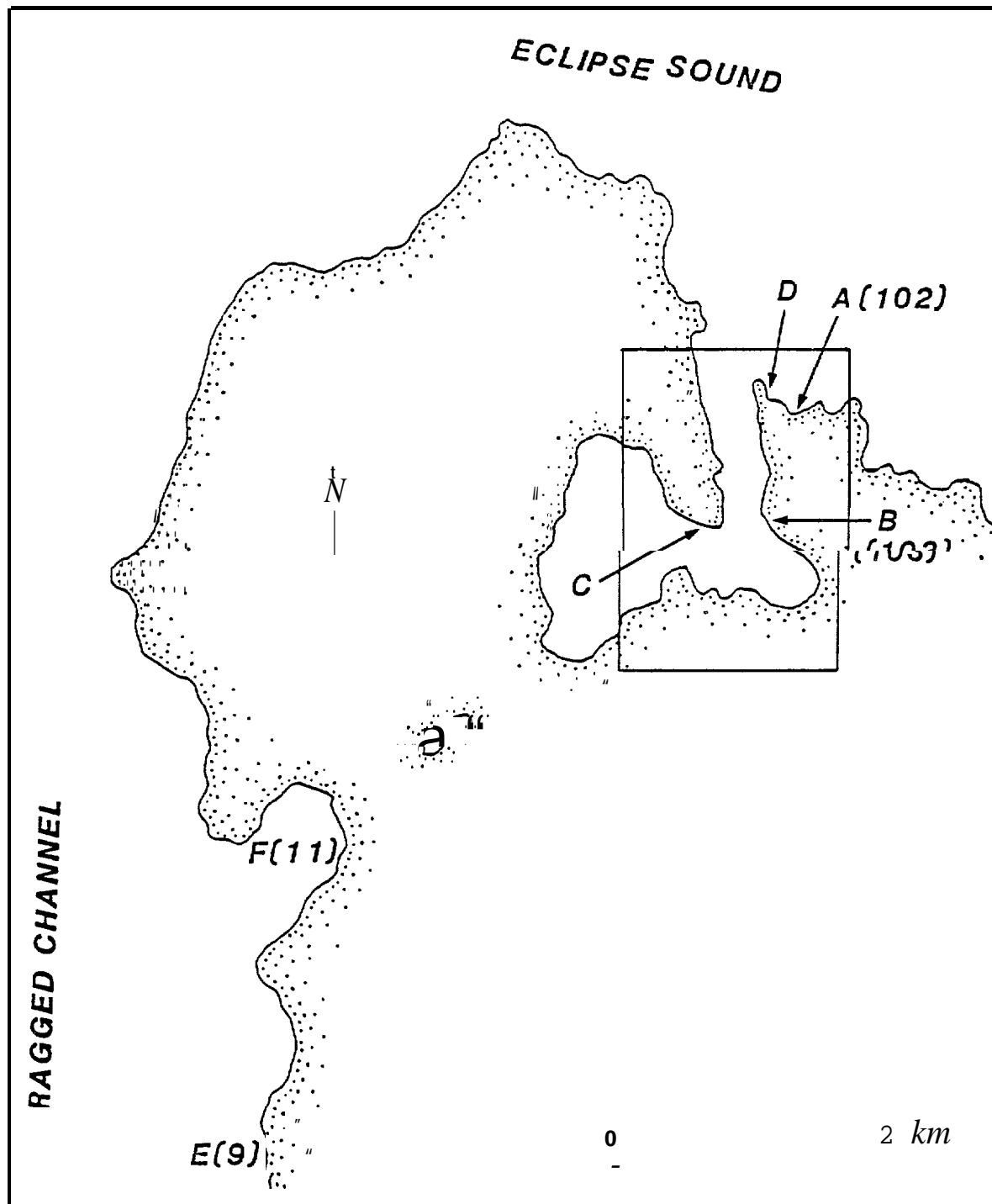
A. 1980 Exposed ("High-Energy") Beach Control Plots: H 1 and H2/Bay 102.

B. 1980 Sheltered ("Low-Energy") Beach Control Plots: L1 and L2/Bay 103.

C. 1980 Backshore Control Plots: T1 and T2.
    1981 Shoreline Countermeasure Experimental and Test Plots.

D. 1980 Norwegian Backshore Control Plots: TE 1 and TE2.
    1981 Norwegian Experimental Plots.

E. Bay 9.

F. Bay 11.

Figure 5.1. Location of Study Beaches.

N→

Cross
Plot

LAND

————————————————————————————— HHWL —————————

ME   CE   CC   MC

D(E)CD(E)E......   SE   SC   D(B)E   D(B)C

————————————————————————————— MHWL —————————

————————————————————————————— LLWL —————————

SEA

10 m

5 m

▨▨▨ **aged crude oil plots**

▦▦▦ **water-in-oil emulsion plots**
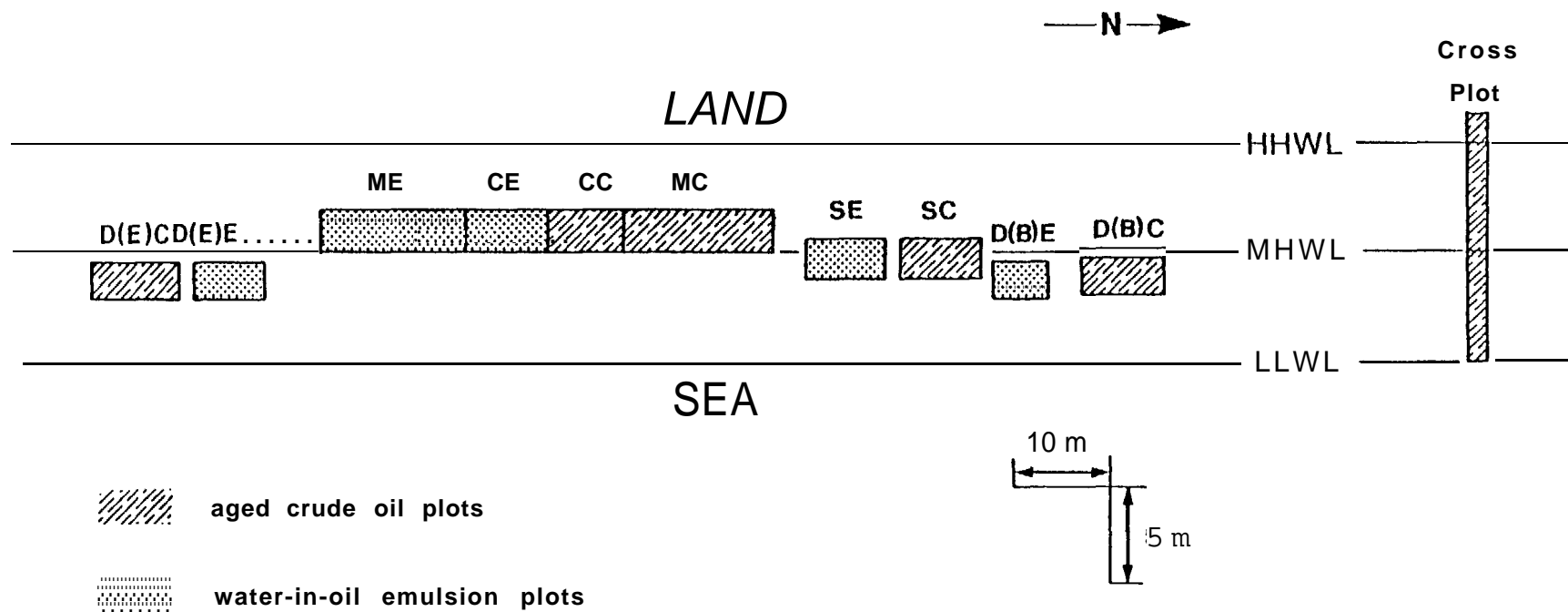
Figure 5.2. Location of 1981 Countermeasure Experimental Plots.

TABLE 5-1

<u>SHORELINE PLOT IDENTIFICATION CODES</u>
(1981 Experiments)

D(E)C	Chemical Dispersion **(Corexit** 7664):	Aged Crude
D(E)E	Chemical Dispersion **(Corexit** 7664):	Emulsion
ME	Mixing: Emulsion	
CE	Control: Emulsion	
cc	Control: Aged Crude	
MC	Mixing: Aged Crude	
SE	Gel: Emulsion	
Sc	Gel: Aged Crude	
D(B)E	Chemical Dispersion (BP 1100X):	Emulsion
D(B)C	Chemical Dispersion (BP 1100X):	Aged Crude

TABLE 5-2

SUMMARY OF 1980 SHORELINE EXPERIMENT TEST PLOTS

TEST PLOT I.D.	TEST AREA (m^2)	LOCATION	SITE DESCRIPTION	TYPE OF OIL SPILLED
H1	40	Bay 102	Upper intertidal open coast, high energy	aged crude
H2	40	Bay 102	Upper intertidal open coast, high energy	50% water/ oil emul- sion
L1	40	Bay 103	Upper intertidal Z-lagoon, low energy	aged crude
L2	40	Bay 103	Upper intertidal Z-lagoon, low energy	50% water/ oil emul- sion
LT1 (=T1)	40	Crude Oil Point	Control plot, backshore area	aged crude
LT2 (=T2)	40	Crude Oil Point	Control plot, backshore area	50% water/ oil emulsion
HT1	4	Bay 102	Control plot, backshore area	aged crude
HT2	4	Bay 102	Control plot, backshore area	50% water/ oil emulsion

TABLE 5-3

SHORELINE STUDY - 1981 PETROLEUM HYDROCARBON CONCENTRATIONS
(sample weight basis)

EXPERI-MENTAL YEAR	PLOT	TIME/LOCATION	I.D.	SATURATED HYDROCARBONS (mg/g)		AROMATIC HYDROCARBONS (mg/g)		TOTAL EXTRACTABLE MATERIAL (mg/g)
				RESOLVED	TOTAL	RESOLVED	TOTAL	
1980	T-1	Surface	S035	4.8	18.8		7.7	44.7
		Subsurface	s036	2.2	9.5	0.5	3.0	23.2
	T-2	Surface	S039	0.8	8.6	0.1	1.1	14.3
		Subsurface	s040	2.2	7.2	0.3	1.8	17.6
	TE-1	Surface	S043	2.4	11.7	0.4	5.1	34.7
		Subsurface	S044	2.3	7.5	0.4	3.4	18.9
	TE-2	Surface	S047	3.6	16.2	0.4	8.7	44.6
		Subsurface	s048	2.6	8.3	0.3	4.4	29.1
	H-1	Surface	S029	0.03	0.2		0.1	0.5
		Subsurface	S030	0.3	1.1	0.03	0.3	1.9
	H-2	Surface	S031	0.8	4.4		1.7	10.1
		Subsurface	s032	0.1	0.5	0.01	0.1	1.0
	L-1	Surface	S013	0.3	1.1		0.1	0.5
		Subsurface	S014	0.7	5.2	0.03	0.3	1.9
	L-2	Surface	S015	0.004	0.02	0.001	0.01	0.08
		Subsurface	s016	0.01	0.1	0.001	0.01	0.3
1981	ME	Post-test	s234	3.9	8.6	0.3	3.8	15.7
		8 days	s252	3.5	8.8	0.4	4.8	18.1
		40 days	S270	0.2	1.2	0.02	0.5	2.6
	CE	Post-test	**SEE SAMPLE ME**					
		8 days	s208	2.4	14.5	0.6	4.6	23.9
		40 days	S2007	0.04	0.3	0.02	0.2	0.9
	MC	Post-test	s225	2.7	10.0	0.4	4.6	21.0
		8 days	S243	0.8	3.4	0.03	0.7	5.5
		40 days	S261	0.3	1.7	0.04	0.9	3.2
	cc	Post-test	**SEE SAMPLE ME **					
		8 days	S279	1.5	2.3	0.3	3.0	10.4
		40 days	s297	0.04	0.4	0.02	0.09	0.7
	D(E)C	Post-test	S146	1.7	3.9	0.2	2.3	8.4
		8 days	s164	0.03	0.1	0.003	0.07	0.3
		40 days	s182	0.01	0.07	0.001	0.03	0.1
	D(E)E	Post-test	S155	0.013	0.12	0.003	0.05	0.3
		8 days	S173	0.091	2.1	0.027	0.9	1.2
		40 days	5188*	7.6	19.8	0.42	4.5	43.4
	SE	Post-test	5335	3.6	18.8		6.8	140
		8 days	S353	4.3	3.8	0.09	0.6	21.3
	Sc	Post-test	S326		7.6	0.4	2.0	16.2
		8 days	5344	0.75	1.6	0.08	0.6	5.0
	D B)E	Post-test	S435	0.7	0.9	0.02	0.07	1.2
		8 days	S452	0.013	0.01	---	0.002	0.02
		40 days	S470	---	0.004	---	0.002	0.01
	D B)C	Post-test	s426	2.0	3.5	0.2	0.9	12.9
		8 days	S444	---	0.004	---	0.002	0.02
		40 days	s461	---	0.007	---	0.003	0.01
	Bay 11 Beach	PR 4 High 9/15/81	M1139	.02	.24	.001	.07	0.4
		PR 4 Med 9/15/81	M1140	.8	13.8	.9	5.1	20.1
		PR 4 Lo 9/15/81	M1141	.2	4.4	.01	1.5	6.1
		PR 6 High 9/15/81	M1142	.8	10.5	.5	3.8	15.6
		PR 6 Med 9/15/81	M1143	.4	5.7	.3	2.1	8.6
		PR 6 Lo 9/15/81	M1144	.2	5.1	.03	1.9	6.9

On the other hand, the high-energy intertidal plot H-1 (aged crude) from Bay 102 contains lower levels of oil (0.3 mg/g, surface; 1.4 mg/g subsurface) than last observed in 1980 (2.1 mg/g). The corresponding plot containing emulsified oil (H-2) contains substantially higher quantities of oil than the H-1 (6.1 mg/g surface; 0.6 mg/g subsurface) but levels roughly equivalent to those last observed in 1980. Considerable differences appear at H-2 between surface and subsurface oil concentrations. The intertidal (low-energy) plot containing aged crude (L-1), showed considerable levels of oil (5.5 mg/g) at depth and lower levels at the surface (1.2 µg/g). Oil concentrations of ~8 mg/g were last observed in 1980.

The concentration changes for the 1981 tests are also shown in Table 5-3. All concentrations decreased with time. The identity of the D(E)E 40-day sample is suspect. Some differences are observed for the mixing (crude and emulsion) and control plots (ME, MC vs. CE, CC), but we cannot determine if these differences are statistically different.

Concentrations of beached oil in Bay 11, the result of an actual landfall of oil, were in the same range (0.2-20 mg/g) after 25 days as those observed at 40 days for the nearshore test plots (Table 5-3).

5.2 Saturated Hydrocarbon Composition

The detailed hydrocarbon composition for the samples and the extent of weathering are best viewed by considering two parameters, the ALK/ISO (alkanes from $n-C_{14}$ through $n-C_{18}$ divided by five key isoprenoids in this boiling range including farnesane, pristane/phytane, and two others), and the SHWR - saturated hydrocarbon weathering ratio:

$$SHWR = \frac{\text{Sum of alkanes from } n\text{-}C_{10} \text{ to } n\text{-}C_{25}}{\text{Sum of alkanes from } n\text{-}C_{17} \text{ to } n\text{-}C_{25}}$$

The ALK/ISO is sensitive to biodegradation as alkanes are preferentially biodegraded (Boehm et al., 1981a; Boehm et al., 1981b; Atlas et al., 1981). The SHWR approaches unity as the lighter components are lost due mainly to evaporation and some dissolution (Boehm and Fiest, 1981a).

The ALK/ISO and SHWR values in the "aged" Lagomedio crude oil are shown in Tables 2-5 and 3-O respectively.

Results for this data set are presented in Table 5-4. In the 1980 test plots the saturates weathered to varying extents between the time the last sampling occurred in 1980 and the 1981 samplings. For example, the SHWR last observed in 1980 for the low-energy backshore test plot (T-1) was ~2.3 (35% of C_{10}-C_{17} lost) and decreased to 1.6 (47% loss) in 1981. A "freshening" of oil was observed at plot H-1 (SHWR=1.7 in 1980; 2.0-2.3 in 1981) indicating plot heterogeneity. A near complete loss of C_{10}-C_{17} saturates occurred at the low-energy intertidal plots L-1 and L-2 in the surface samples (SHWR 1.0). Note, however, that less weathered oil, SHWR 1.5-2.0, is found at depth in these plots, in the case of L-1 corresponding to an increase in oil concentration as well.

Biodegradation has only occurred to a large extent in the L-2 (surface) plot (ALK/ISO = 1.1). Concentrations are very low here, indicating that if biodegradation occurs in the test plots in general, its effects are masked by high oil concentrations.

Varying degrees of weathering are observed for the
1981 experiment plots but never more than ~70 percent
(SHWR=1.4) and usually ~50% (SHWR=2.0). Biodegradation
is a minor weathering process in these samples.

Note that where light petroleum additives are important
components of the test mixture as in the gel plots (SE, SC)
and the BP dispersant plots (D(B)E; D(B)C), SHWR and ALK/ISO
values exceed the original oil due to contributions of
these additives to these ratios. Rapid weathering of these
light hydrocarbons is observed for these test plots (e.g.,
SHWR goes from 20 to 1.2 at D(B)E). Thus where there is a
great abundance of $C_{10}-C_{17}$ components such as in No. 2
fuel oil for example, evaporative weathering is a quantita-
tively more important removal mechanism than for an aged
crude oil.

The observations for the weathering of oil in the
shoreline experiments is supported by the Bay 11 beached
oil measurements (see Table 5-4). Beached oil, after about
one month of exposure, has weathered to the point where 60
to 75 percent of the alkanes lower than C_{17} have been lost
through evaporation (and solution) but biodegradation is
undetected (ALK/ISO$\overset{\sim}{=}$2.3-2.8)

The GC^2 chemical composition of the test oils is
very similar (Table 5.2), all oils having SHWR ratios $\overset{\sim}{-}$2.5.
Thus there would be little variability between the composition
of test oils at the time of application.

5.3 Aromatics (GC^2/MS)

Samples from several of the test plots were analyzed by
GC^2/MS to determine the weathering profile of the residual

aromatic hydrocarbons.   The analytical results expressed
as the aromatic weathering ratio (AWR) are presented in
Table 5-4.

$$AWR = \frac{\Sigma(\Sigma alkyl\ benzenes + \Sigma naphthalenes + \Sigma phenanthrenes + \Sigma fluorenes + \Sigma dibenzothiophenes)}{\Sigma(\Sigma phenanthrenes + \Sigma dibenzothiophenes)}$$

The AWR is similar in concept to the SHWR and approaches
unity as the more volatile and soluble compounds are weathered
from the samples.   As can be seen in Table 5-4, additional
weathering has occurred between 1980 and 1981.   When last
sampled in 1980, the AWR at T-1 was 3.1 (16% weathered) and
in 1981 the value was 2.0 (60% weathered).   Similarly, at
site L-1 the AWR was 3.1 in 1980 and was altered to 1.4
(84% weathered) in 1981 indicating loss of the one and two
ringed aromatic compound families.

Samples from several of the 1981 test plots were
analyzed by GC^2/MS after 40 days of exposure.   AWR values
varied from 2.8 at D(E)E (28% weathered) to 1.4 at D(B)C
(84% weathered), the latter of course reflecting weathering
of the Lagomedio crude oil and the light petroleum addition
in the BP dispersant.   A time series at D(E)C indicated that
the aromatic weathering was rapid between O and 8 (AWR 3.0
to 1.9) days and changed little in the next month (AWR = 1.9
after 40 days).

TABLE 5-4

SHORELINE STUDY-1981 PETROLEUM HYDROCARBON WEATHERING PARAMETERS

	PLOT	TIME	SHWR	ALK/ISO	AWR
1980 plots	T-1	Surface	1.6	2.1	2.0
		Subsurface	1.7	2.5	---
		(1980 sample)	2.3-2.4	2.1-2.3	3.1
	T-2	Surface	1.6	2.4	3.1
		Subsurface	2.0	2.6	---
		(1980 sample)	1.8-2.3	2.5-3.0	
	TE-1	Surface	1.5	3.1	---
		Subsurface	2.0	3.7	---
	TE-2	Surface	1.2	2.4	---
		Subsurface	1.7	2.7	---
	H-1	Surface	2.0	1.6	---
		Subsurface	2.3	2.1	---
		(1980 sample)	1.6-1.8	2.6-2.8	---
	H-2	Surface	2.1	2.4	---
		Subsurface	2.2	2.8	---
		(1980 sample)	1.2-1.8	2.1-2.4	---
	L-1	Surface	1.1	1.9	---
		Subsurface	2.0	2.4	1.4
		(1980 sample)	2.3-2.5	2.6	3.1
	L-2	Surface	1.0	1.1	---
		Subsurface	1.4	1.9	---
		(1980 sample)	2.0-2.2	2.6-2.8	
1981 plots	ME	Post-test	3.0	2.7	---
		+ 8 days	2.1	4.0	---
		+ 40 days	2.0	2.1	2.4
	CE	+ 8 days	2.3	2.6	---
		+ 40 days	1.4	2.7	---
	MC	+ 8 days	1.8	2.1	---
		+ 40 days	2.0	2.5	---
	cc	+ 8 days	2.6	2.6	---
		+ 40 days	1.6	1.6	---
	MC	Post-test	3.0	2.1	---

TABLE 5-4 (CONT.)

	PLOT	TIME (LOCATION)	SHWR	ALK/I SO	AWR
1981 plots	D(E)C	Post-test	2.3	3.2	3.0
		+ 8 days	1.9	4.1	1.9
		+ 40 days	1.9	2.6	1.9
	D(E)E	Post-test	1.9	3.2	---
		+ 8 days	1.9	2.8	---
		+ 40 days			2.8
	SE	Post-test	105	5.0	---
		+ 8 days	5.2	8.1	---
	SC	Post-test			---
		+ 8 days	6.6	4.2	---
	D(B)E	Post-test	20.1	5.3	---
		+ 8 days	3.3	4.5	---
		+ 40 days	1.2	1.2	1.4
	D(B)C	Post-test	7.0	3.8	---
		+ 8 days	1.4	2.9	---
		+ 40 days	2.6	2.7	1.8
Bay 11	PR 4	High	1.2	2.3	---
		Med	1.9	2.7	---
		Low	1.5	2.8	---
	PR 6	High	1.5	2.9	---
		Med	1.6	2.7	---
		Low	1.8	2.7	---
Oils					
	S703a	ME	2.3	2.4	---
	S704a	MC	2.4	2.4	---
	S704b	MC	2.2	2.4	---
	S704C	MC	2.4	2.4	---
	S705	Sc	2.2	2.5	---
	s712	D(B)C	2.7	2.4	---

SHWR = saturated weathering ratio; varies from ~3.0 to 1.0; higher values due to diesel or kerosene inputs or to biogenic inputs

AWR = aromatic weathering ratio; by GC/MS; varies from ~3.5 to 1.0

ALK/ISO = biodegradation ratio; varies from ~2.5 to 0 as alkanes are preferentially degraded; may be higher where kerosene inputs are noted

SECTION SIX

SECTION SIX

DISCUSSION (SHORELINE STUDY)

     Several generalities can be derived from the results of
the shoreline applications of oil. Firstly and quite
importantly, it appears as if the rate of application of oil
to the beach was quite realistic as the shoreline dosings of
oil were similar to those quantities actually beached during
the Bay 11 spill. Thus we might expect realistic post-beaching
weathering rates to be observed.

     Indeed over the 30-40 days after application of oil to
the shoreline test plots the extent of weathering, mainly
due to evaporation, is similar to that observed with the Bay
11 beached oil. Microbial degradation is not a significant
removal mechanism during this period. However, at lower oil
levels (e.g., plot CE, 40 days; or Bay 11, PR 4, High) the
extent of weathering is accelerated including microbial
degradation. For example, at CC (+40 days) oil levels are
lower (0.5 mg/g) and microbial degradation is observed to
begin to occur (ALK/ISO = 1.6). One year after the appli-
cation of oil at plot L-2, levels of oil are quite low and
weathering quite advanced (SHWR = 1.0; ALK/ISO = 1.1).
Subsurface oil on the 1980 plots seems to be better preserved
than oil exposed to surface processes (i.e., evaporation).

     In the 1981 test plots to which kerosene-based additives
are added, the low molecular weight hydrocarbons which are
characteristic of the kerosene (or diesel) additive (and
which cause the initially high value for the SHWR parameter)
are lost due to weathering. For example the low molecular
weight saturates, part of the gel added to plot SE causes an

initial SHWR of 105. Within 8 days low boiling components
are much reduced (5.2) but are still present in relative
quantities greater than the initial oil (SHWR = 3.5). Thus
if the abundance of low molecular weight compounds are an
indicator of toxic properties of the oil one might conclude
that the gel/oil mixture is more toxic than oil alone.
However, the gel/oil mixture's availability to intertidal
animals, for example, may be less than the oil itself.
These factors may balance, but in any event must be viewed
and compared vis-a-vis the toxicity of a resultant oil/
dispersion mixture. It also appears that the BP dispersant
applied in plots D(B)E and D(B)C contains light saturates and
aromatics (kerosene) (SHWR = 20). That the oil in the D(B)
plots is rapidly removed from the shoreline is noted by the
decrease in beach-bound oil concentrations. However, the fate
of this oil in the intertidal system must be carefully
considered, especially due to the presence of significant
amounts of the low boiling aromatic components, to factor in
any intertidal impacts (or lack thereof) into the overall
decision as to the useage of these dispersants to remove oil
from the beach face.

SECTION SEVEN

SECTION SEVEN

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APPENDIX **A**

APPENDIX A

STATISTICAL SUMMARIES

TABLE A.1

STATISTICAL SUMMARY OF TISSUE PLOT SEDIMENT DATA (UV/F)

					UV/F OIL CONCENTRATIONS (μg/g)		
						95% CONFIDENCE LIMITS	
GROUP	BAY	SAMPLING	STRATUM	N	GEOMETRIC MEAN	Lower	Upper
1	11	Pre-spill	7m	4	.55	.13	1.1
2	11	1st post-spill	7m	5	.18	.00	.42
3	11	2nd post-spill	7m	5	1.1	.46	1.9
4	10	Pre-spill	7m	4	0.49	.16	.92
5	10	1st post-spill	7m	5	0.88	.44	1.5
6	10	2nd post-spill	7m	5	1.7	.73	3.3
7	9	Pre-spill	7m	4	0.38	-.13	1.2
8	9	1st post-spill	7m	5	2.1	1.5	2.7
9	9	2nd post-spill	7m	5	9.0	5.2	15.
10	7	Pre-spill	7m	4	0.43	.04	.97
11	7	1st post-spill	7m	5	0.67	.45	.92
12	7	2nd post-spill	7m	5	1.1	.63	1.7
13	11	Pre-spill	3m	4	0.22	.06	.40
14	11	1st post-spill	3m	5	0.16	.04	.30
15	11	2nd post-spill	3m	5	0.70	.17	1.5
16	10	Pre-spill	3m	4	0.45	.32	.59
17	10	1st post-spill	3m	5	1.40	1.1	1.9
18	10	2nd post-spill	3m	5	0.73	0.0	2.0
19	9	Pre-spill	3m	4	0.34	.13	.57
20	9	1st post-spill	3m	5	3.1	1.9	4.7
21	9	2nd post-spill	3m	5	5.3	2.4	11.
22	7	Pre-spill	3m	4	0.36	.01	1.5
23	7	1st post-spill	3m	5	0.34	.29	.39
24	7	2nd post-spill	3m	5	0.45	-.09	1.3

TABLE A. 2

STATISTICAL COMPARISON FOR TISSUE PLOT SEDIMENT DATA **(UV/F)**
WITHIN BAY COMPARISONS

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | | | | |
| | 7M DEPTH STRATUM | | 3M DEPTH STRATUM | | |
	1ST POST-SPILL	2ND POST-SPILL	1ST POST-SPILL	2ND POST-SPILL	3M VERSUS 7M COMPARISON
Bav 11					
Pre-spill	.05	.13	.42	.07	.07
1st post-spill		<.01		.03	.76
2nd post-spill					.32
Bav 10					
Pre-spill	**.12**	.02	<.01	.45	.74
1st post-spill		.08		.14	.05
2nd post-spill					.11
Bay 9					
Pre-spill	<.01	<.01	<.01	<.01	.85
1st post-spill		<.01		.12	.07
2nd post-spill					1.14
Bay 7					
Pre-spill	.20	.03	.82	.78	.73
1st post-spill		.05		.64	<.01
2nd post-spill					.08

TABLE A. 3

STATISTICAL COMPARISON FOR TISSUE PLOT SEDIMENT DATA (UV/F) AMONG BAY COMPARISONS

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | | | | | |
| | 7M DEPTH STRATUM | | | 3M DEPTH STRATUM | | |
	BAY 10	BAY 9	BAY 7	BAY 10	BAY 9	BAY 7
Pre-spill						
Bay 11	.77	.52	.59	.02	.23	.33
Bay 10		.65	.77		.2"2	.57
Bay 9			.83			.86
Bay 7						
1st Post-Spill						
Bay 11	<.01	<.01	<.01	<.01	<.01	.01
Bay 10		<.01	.30		<.01	<.01
Bay 9			**<.01**			<.01
Bay 7						
2nd Post-Spill						
Bay 11	**.21**	**<.01**	**.91**	**.93**	<.01	.48
Bay 10		<.01	*19		<.01	.51
Bay 9			<.01			<.01
Bay 7						

TABLE A.4

STATISTICAL SUMMARY OF TISSUE PLOT SURFACE FLOC DATA **(UV/F)**

UV/F OIL CONCENTRATIONS (µg/g)

GROUP	BAY	SAMPLING	STRATUM	N	GEOMETRIC MEAN	95% CONFIDENCE LIMITS Lower	Upper
1	11	Pre-spill	7m	2	0.96	**-.61**	2.1
2	11	1st post-spill	7m	5	0.23	**-.02**	.53
3	11	2nd post-spill	7m	5	0.11	**.09**	1.6
4	10	Pre-spill	7m	2	0.19	**.07**	.33
5	10	1st post-spill	7m	5	4.0	2.0	7.2
6	10	2nd post-spill	7m	5	0.068	.05	.08
7	9	Pre-spill	7m	2	0.040	-.08	.18
8	9	1st post-spill	7m	5	9.70	2.8	29.
9	9	2nd post-spill	7m	5	0.10	.01	.21
10	7	Pre-spill	7m	No samples			—
11	7	1st post-spill	7m	5	0.12	.01	.24
12	7	2nd post-spill	7m	5	0.024	.01	.04
13	11	Pre-spill	3m	2	0.084	-.28	.64
14	11	1st post-spill	**3m**	**No** samples			
15	11	2nd post-spill	**3m**	5	0.071	.02	.13
16	10	Pre-spill	**3m**	2	0.10	-.02	.24
17	10	1st post-spill	3m	1	0.071		
18	10	2nd post-spill	3m	5	0.050	.02	.08
19	9	Pre-spill	3m	2	0.035	-.14	.24
20	9	1st post-spill	3m	5	4.26	2.0	8.3
21	9	2nd post-spill	3m	4	0.10	.04	.18
22	7	Pre-spill	3m	No samples			—
23	7	1st post-spill	3m	5	0.066	.04	.09
24	7	2nd post-spill	3m	5	0.040	.00	.08

STATISTICAL COMPARISON FOR SURFACE FLOC DATA (UV/F) WITHIN BAY COMPARISON

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)				
	7M DEPTH STRATUM		3M DEPTH STRATUM		
	1ST POST-SPILL	2ND POST-SPILL	1ST POST-SPILL	2ND POST-SPILL	3M VERSUS 7M COMPARISON
Bav 11					
Pre-spill	.45	.99	No data	.74	.97
1st post-spill		.26		No data	.03
2nd post-spill·					.41
Bay 10					
Pre-spill	<.01	<.01	No data	.03	.02
1st post-spill		<.01		No data	No data
2nd post-spill					.14
Bay 9					
Pre-spill	.01	.32	.01	.11	.80
1st post-spill		<.01		<.01	.13
2nd post-spill					.65
Bay 7					
Pre-spill	No data	No data	No data	No data	No data
1st post-spill		.06		.18	.28
2nd post-spill					.36

TABLE A.6

STATISTICAL COMPARISON FOR SURFACE FLOC DATA (UV/F) AMONG BAY COMPARISON

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)					
	7M DEPTH STRATUM			3M DEPTH STRATUM		
	BAY 10	BAY 9	BAY 7	BAY 10	BAY 9	BAY 7
Pre-spill						
Bay 11	.66	.58	No data	.72	.31	No data
Bay 10		.01	No data		.07	No data
Bay 9			No data			No data
Bay 7						
1st Post-sDill						
Bay 11	**<.01**	<.01	.30	No data	No data	No data
Bay 10		.10	<.01		.01	.45
Bay 9			<.01			<.01
Bay 7						
2nd Post-Spill						
Bay 11	.30	.97	.04	.34	.74	.23
Bay 10		.35	<.01		.28	.58
Bay 9			.05			.20
Bay 7						

TABLE A.7

STATISTICAL SUMMARY OF **BENTHIC** BIOLOGY SEDIMENT DATA **(UV/F)**

| | | | | | UV/F OIL CONCENTRATIONS (μg/g) | | |
| | | | | | GEOMETRIC MEAN | 95% CONFIDENCE LIMITS Lower | Upper |
GROUP	BAY	SAMPLING	STRATUM	N			
1	11	2nd post-spill	7m	12	3.8	2.5	5.8
2	**10**	2nd post-spill	**7m**	**13**	1.6	1.1	2.2
3	**9**	2nd post-spill	7m	13	3.8	2.6	5.5
4	**7**	2nd post-spill	7m	12	1.2	.77	1.6
5	11	2nd post-spill	3m	12	0.90	.43	1.5
6	10	2nd post-spill	**3m**	13	**0.99**	.48	**1.7**
7	9	2nd post-spill	3m	13	2.7	1.6	4.2
8	7	2nd post-spill	3m	13	0.80	.45	1.2

TABLE A. 8

STATISTICAL COMPARISON OF **BENTHIC** BIOLOGY SEDIMENT DATA **(UV/F)**
WITHIN BAY COMPARISONS

BENTHIC BIOLOGY DATA	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)		
	7M DEPTH STRATUM TISSUE PLOT DATA	3M DEPTH STRATUM TISSUE PLOT DATA	3M VERSUS 7M COMPARISON (BENTHIC BIOLOGY DATA)
Bay 11			
2nd post-spill	<.01	.18	<.01
Bay 10			
2nd post-spill	.01	.19	.01
Bay 9			
2nd post-spill	<.01	.04	<.01
Bay 7			
2nd post-spill	.04	.07	.04

STATISTICAL COMPARISON OF <u>BENTHIC</u> BIOLOGY SEDIMENT DATA <u>(UV/F)</u>
<u>AMONG BAY COMPARISONS</u>

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)					
	7M DEPTH STRATUM			3M DEPTH STRATUM		
	BAY 10	BAY 9	BAY 7	BAY 10	BAY 9	BAY 7
2nd Post-Spill						
Bay 11	<.01	1.0	<.01	.71	<.01	.61
Bay 10		<.01	.01		**<.01**	**.39**
Bay 9			**<.01**			**<.01**
Bay 7						

TABLE A.10

STATISTICAL SUMMARY OF Mya _truncata_ DATA (UV/F)

					UV/F OIL CONCENTRATIONS (μg/g)		
						95% CONFIDENCE LIMITS	
GROUP	BAY	SAMPLING	STRATUM	N	GEOMETRIC MEAN	Lower	Upper
1	11	Pre-spill	7m	5	0.43	.33	.53
2	11	1st post-spill	7m	5	2.0	1.2	3.1
3	11	2nd post-spill	7m	5	93.	73.	120
4	10	Pre-spill	7m	5	0.57	.42	.74
5	10	1st post-spill	7m	5	277	180	420
6	10	2nd post-spill	7m	5	157	110	230
7	9	Pre-spill	7m	5	0.35	.22	.49
8	9	1st post-spill	7m	5	121	51	290
9	9	2nd post-spill	7m	5	114	90	140
10	7	Pre-spill	7m	5	0.34	.21	.48
11	7	1st post-spill	7m	5	114	64	210
12	7	2nd post-spill	7m	5	47	31	70
13	10	Pre-spill	3m	5	0.78	.55	1.0
14	10	1st post-spill	3m	5	368	290	460
15	10	2nd post-spill	3m	5	131	96.	178
16	9	Pre-spill	3m	5	0.40	.25	.56
17	9	1st post-spill	3m	5	215	130	350
18	9	2nd post-spill	3m	5	135	120	150

TABLE A11

STATISTICAL COMPARISON OF Mya truncata DATA **(UV/F)**
WITHIN BAY COMPARISONS

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | | | | |
| | 7M DEPTH STRATUM | | 3M DEPTH STRATUM | | |
	1ST **POST-** SPILL	2ND **POST-** SPILL	1ST **POST-** SPILL	2ND **POST-** SPILL	3M VERSUS 7M COMPARISON
Bay 11					
Pre-spill	<.01	<.01			
1st post-spill		**<.01**			
2nd post-spill					
Bay 10					
Pre-spill	<.01	<.01	<.01	<.01	*.08*
1st post-spill		.02		<.01	*.14*
2nd post-spill					*.34*
Bay 9					
Pre-spill	<.01	<.01	<.01	<.01	.50
1st post-spill		**.84**		.04	.15
2nd post-spill					.46
Bay 7					
Pre-spill	<.01	<.01			
1st post-spill		.01			
2nd post-spill					

TABLE A.12

STATISTICAL COMPARISON OF Mya truncata DATA **(UV/F)**
AMONG BAY COMPARISONS **(µg/g)**

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | | | |
| | 7M DEPTH STRATUM | | | 3M DEPTH STRATUM |
	BAY 10	BAY 9	BAY 7	BAY 9
Pre-spill				
Bay 11	.06	.21	.18	.01
Bay 10		.02	.01	
Bay 9			<.01	
Bay 7				
1st Post-Spill				
Bay 11	<.01	<.01	<.01	
Bay 10		.04	.01	.03
Bay **9**			**.87**	
Bay 7				
2nd Post-Spill				
Bay 11	.01	.14	<.01	
Bay 10		.08	<.01	
Bay 9			<.01	.83
Bay 7				

TABLE A.13

STATISTICAL SUMMARY OF *Serripes groenlandicas* DATA (UV/F)

GROUP	BAY	SAMPLING	STRATUM	PROCEDURE	N	GEOMETRIC MEAN	95% CONFIDENCE LIMITS Lowe r	Upper
1	11	Pre-spill	7m	Air lifted	1			
2	11	1st post-spill	7m	Air lifted	4	6.0	.19	41
3	11	2nd post-spill	7m	Air lifted	3	394	200	780
4	10	Pre-spill	7m	Air lifted	5	1.4	.40	3.0
5	10	1st post-spill	7m	Air lifted	5	278	220	350
6	10	2nd post-spill	7m	Air lifted	5	149	130	170
7	9	Pre-spill	7m	Air lifted	4	0.68	-.02	1.9
8	9	1st post-spill	7m	Air lifted	5	482	340	680
9	9	2nd post-spill	7m	Air lifted	5	116	69	190
10	7	Pre-spill	7m	Air lifted	3	1.2	1.2	1.3
11	7	1st post-spill	7m	Air lifted	4	517	360	750
12	7	2nd post-spill	7m	Air lifted	4	73	31	170
13	10	1st post-spill	7m	Hand picked	4	329	240	460
14	10	2nd post-spill	7m	Hand picked	4	141	110	180
15	9	1st post-spill	7m	Hand picked	5	186	110	330
16	9	2nd post-spill	7m	Hand picked	5	97	59	160
17	10	1st post-spill	3m	Hand picked	5	698	500	970
18	9	2nd post-spill	3m	Hand picked	5	160	120	210

UV/F OIL CONCENTRATIONS (µg/g)

TABLE A.14

STATISTICAL COMPARISON OF Serripes groenlandicas DATA **(UV/F)**
WITHIN BAY COMPARISONS

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | | | |
| | 7M DEPTH STRATUM | | 3M DEPTH STRATUM | |
	1ST POST- SPILL	2ND **POST-** SPILL	1ST POST- SPILL	HAND VERSUS AIRLIFT
Bay 11				
Pre-spill	N/A	N/A		
1st post-spill		<.01		
2nd post-spill				
Bay 10				
Pre-spill	<.01	<.01		
1st post-spill		<.01	<.01	.25
2nd post-spill				.85
Bay 9				
Pre-spill	<.01	<.01		
1st post-spill		<.01		<.01
2nd post-spill			.04	.55
Bay 7				
Pre-spill	<.01	<.01		
1st post-spill		<.01		
2nd post-spill				

TABLE A.15

STATISTICAL COMPARISON OF AIRLIFTED Serripes groenlandicas
DATA (UV/F) AMONG BAY COMPARISONS

PROBABILTY OF SIMILARITY (TWO-TAILED T-TEST)

7M DEPTH STRATUM

	BAY 10	BAY 9	BAY 7
Pre-spill			
Bay 11/10	N/A	N/A	N/A
Bay 10	–	0.20	.15
Bay 9	–	–	0.30
Bay 7	–	–	–
1st Post-Spill			
Bay 11	<.01	<.01	<.01
Bay 10	–	.01	<.01
Bay 9	–	–	0.70
Bay 7	–	–	–
2nd Post-Spill			
Bay 11	<.01 ●III	<.01 ●II	<.01
Bay 10	–	.22	.02
Bay 9	–	–	.20
Bay 7	–	–	–

TABLE A. 16

STATISTICAL SUMMARY OF Macoma calcarea DATA (UV/F)

| | | | | | UV/F OIL CONCENTRATIONS (µg/g) | | |
| | | | | | GEOMETRIC MEAN | 95% CONFIDENCE LIMITS Lower | Upper |
VARIABLE	BAY	SAMPLING	STRATUM	N			
1	11	Pre-spill	7m	4	2.5	.05	10.
2	11	1st post-spill	7m	5	24.5	14.	42.
3	11	2nd post-spill	7m	4	246	76.	790.
4	10	Pre-spill	7m	5	2.1	1.0	3.6
5	10	1st post-spill	7m	5	406	241.	680.
6	10	2nd post-spill	7m	5	440	250.	760.
7	9	Pre-spill	7m	5	0.73	.33	1.2
8	9	1st post-spill	7m	5	74.9	36.	150.
9	9	2nd post-spill	7m	5	836	610.	1140.
10	7	Pre-spill	7m	5	1.0	.88	1.2
11	7	1st post-spill	7m	5	82.1	60.	112.
12	7	2nd post-spill	7m	5	85.5	39.	190.

TABLE A.17

STATISTICAL COMPARISON OF Macoma calcarea DATA (UV/F)
WITHIN BAY COMPARISONS

| | PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST) | |
| | 7M DEPTH STRATUM | |
	1ST POST-SPILL	2ND POST SPILL
Bay 11		
Pre-spill	<.01	<.01
1st post-spill		<.01
2nd post-spill		
Bay 10		
Pre-spill	<.01	<.01
1st post-spill		.78
2nd post-spill		
Bay 9		
Pre-spill	<.01	<.01
1st post-spill		**<.01**
2nd post-spill		
Bay 7		
Pre-spill	<.01	**<.01**
1st post-spill		.90
2nd post-spill		

TABLE A.18

STATISTICAL COMPARISON OF Macoma calcarea DATA (UV/F) AMONG BAY COMPARISONS

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)		
	7M DEPTH STRATUM		
	BAY 10	BAY 9	BAY 7
Pre-spill			
Bay 11	*0.80*	0.08	0.15
Bay 10		.01	.03
Bay 9			<.01
Bay 7			
1st Post-Spill			
Bay 11	<.01	.01	<.01
Bay 10		<.01	<.01
Bay 9			*.76*
Bay 7			
2nd Post-Spill			
Bay 11	0.20	.01	.06
Bay 10		.02	<.01
Bay 9			<.01
Bay 7			

TABLE A.19

STATISTICAL SUMMARY OF ASTARTE BOREALIS DATA (UV/F)

VARIABLE	BAY	SAMPLING	STRATUM	N	GEOMETRIC MEAN	95% CONFIDENCE LIMITS Lower	95% CONFIDENCE LIMITS Upper
1	11	Pre-spill	7m	5	.47	.13	.92
2	11	1st post-spill	7m	5	2.7	2.2	3.4
3	11	2nd post-spill	7m	4	140	50.	390.
4	10	Pre-spill	7m	5	0.43	.25	.64
5	10	1st post-spill	7m	4	364	320.	410.
6	10	2nd post-spill	7m	5	310	210.	460.
7	9	Pre-spill	7m	4	0.81	.44	1.3
8	9	1st post-spill	7m	5	463	270.	800.
9	9	2nd post-spill	7m	5	171	88.	330.
10	7	Pre-spill	7m	4	22	.38	6.4
11	7	1st post-spill	7m	5	51	12.	210.
12	7	2nd post-spill	7m	4	56	31.	140.

The UV/F OIL CONCENTRATIONS (µg/g) header spans the GEOMETRIC MEAN and 95% CONFIDENCE LIMITS columns.

TABLE A.20

STATISTICAL COMPARISON OF Astarte Borealis DATA **(UV/F)**
WITHIN BAY COMPARISONS

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)	
	7M DEPTH STRATUM	
	FIRST POSTSPILL	SECOND POSTSPILL
Bay 11		
Prespill	<0.01	<0.01
First Postspill		<0.01
Second **Postspill**		
Bav 10		
Prespill	<0.01	<0.01
First **Postspill**		<0.01
Second **Postspill**		
Bay 9		
Prespill	<0.01	<0.01
First **Postspill**		0.01
Second **Postspill**		
Bay 7		
Prespill	<0.01	<0.01
First **Postspill**		0.89
Second **Postspill**		

TABLE A.21

<u>STATISTICAL COMPARISON OF Astarte Borealis</u>
<u>DATA (UV/F) AMONG BAY COMPARISONS</u>

	PROBABILITY OF SIMILARITY (TWO-TAILED T-TEST)		
	7M DEPTH STRATUM		
	BAY 10	BAY 9	BAY 7

Pre-spill

Bay 11	*0.78*	0.15	0.02
Bay 10		0.03	0.07
Bay 9			0.09
Bay 7			

1st Post-Spill

Bay 11	<0.01	<0.01	<0.01
Bay 10		0.33	0.01
Bay 9			<0.01
Bay 7			

2nd Post-Spill

Bay 11	0.04	0.63	0.08
Bay 10		0.07	<0.01
Bay 9			0.02
Bay 7			